REACTIONS OF METHYLENE

Thesis submitted for the degree of Doctor of Philosophy

by

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CONTENTS

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LIST OF TABLES

PREFACE

The research reported in this thesis concerns some reactions of the simplest organic entity - methylene.

Reactivity of this species, indicative of its radical character was the reason why, though its presence in many chemical reactions was postulated in the last decade of the 19th century, the confirmation of its existence came much later, in the thirties of the present one, when the new techniques of investigation of unstable compounds such as the Paneth-mirror technique, were developed.

From then till the 1950's the methylene reactions were the domain of organic chemists, who studied them mainly for their preparative applications.

Invention of new analytical methods, such as mass spectrometry and gas chromatography, has enabled us to investigate these reactions quantitatively, with the prospect of elucidating the structure of methylene.

The results of this work on reactions of methylene with 1,3 butadiene, butene-1, pentene-1 and tetrafluoroethylene are included in the first part of this thesis which attempts to be a survey of the methylene reactions, and can thus be regarded as the joint introduction and discussion.

As the biradical nature of methylene, which would correspond to its triplet state, is still a matter of controversy and as, in many reactions methylene shows both radical and non-radical behaviour, no special division will be made between its monoradical reactions and those peculiar to

biradicals, all reactions being classified into:-

a) Insertion

b) Abstraction and Displacement,

and c) Addition reactions.

The conclusions about the structure of methylene supported by studies of its reactions will be discussed in the paragraph "Structure of Methylene".

Unimolecular reactions of the cyclopropane derivatives, formed by the addition of methylene to a double bond of defins are the subject of the last paragraph in this survey.

CHAPTER 1

REACTIONS OF METHYLENE

1.1 OCCURRENCE, DETECTION AND PHYSICAL PROPERTIES OF METHYLENE

The presence of methylene in the intermediate stages of the reactions of oxidation,[1,2] decomposition of hydrocarbons[3,4] and polymerization[5] has been a subject of much speculation during the last 50 years.

The first positive proof of its existence was obtained in 1935 by Norrish Crone and Saltmarsh[6], and independently by Ross and Kistiakowsky[7], from the photochemical decompositions of keten and diazomethane. The fact that the absorption region most responsible for the photodissociation corresponded to the absorption band of a carbonyl group together with the formation of ethylene and carbon monoxide as products of the decomposition, led the authors to the conclusion that a primary act in the dissociation of keten was the splitting of the molecule according to the reaction:

$$CH_2{=}{=}CO + h\nu \rightarrow CH_2 + CO$$

followed by:

$$CH_2 + CH_2{=}{=}CO \rightarrow C_2H_4 + CO$$

Similar studies on the decomposition of diazomethane[8] showed that also in this case methylene was formed in the first stage of the reaction. Formation of methylene during the photo - and thermal dissociations of keten and diazomethane was then confirmed by the most direct method in the studies of radicals - the mirror removal technique[9,10]. It was found that tellurium, selenium, arsenic and antimony mirrors were removed by the products of decomposition, with the formation of appropriate formaldehydes (e.g. telluro-formaldehyde from a tellurium mirror) in mono- or polymeric forms.

CHAPTER 1

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The occurrence of methylene in the thermal decompositions of hydrocarbons, in particular of methane, was a subject of much controversy. In an early paper on the thermal decomposition of methane Kassel[5] suggested that the most probable reaction to take place was:

$$CH_4 \longrightarrow CH_2 + H_2$$

Following this idea two groups of workers studied products of this decomposition by the mirror-technique obtaining contradictory results. Thus Rice and Dodey[11] found only pure dimethyltelluride, indicative of the presence of methyl radicals, whereas Belchetz et al[12] claimed the presence of methylene in this reaction obtaining methylene iodide from iodine mirrors and some compound, which they identified as telluroformaldehyde, from tellurium mirrors. These discrepancies were ascribed to different experimental conditions in the two investigations: it was suggested that methylene formed in the primary step was able to abstract a hydrogen atom giving a methyl radical. When the distance from the filament, on which the decomposition was taking place, to the mirror was bigger than the mean free path of methylene only methyl could be detected, when this distance was smaller - methylene appeared.

Difficulties in unambiguous identification of products in mirror-removal experiments, and non-reproducibility of Belchetz' results cast some doubt on the presence of methylene in the decomposition of methane, and this problem still remains open. In the case of the decomposition of higher hydrocarbons, however, the possibility of the presence of methylene seems to be definitely excluded.

Other cases where the presence of methylene was detected are an electrical discharge through methane, keten and diazomethane[13,14], and the reaction of atomic sodium with methylenehalide[15];

$$2Na + CH_2X_2 \longrightarrow CH_2 + 2NaX$$

It was reported in the last months that methylene can also be produced from the photolysis of diazirine (cyclodiazomethane) according to the reaction[101]:

$$CH_2 \begin{matrix} N \\ \| \\ N \end{matrix} + h\nu \longrightarrow CH_2 + N_2$$

Spectroscopic evidence for the existence of methylene was lacking till 1959, when Herzberg and Shoosmith[16] ascribed a group of lines near 1400 Å, found in the flash photodysis of diazomethane to the spectrum of methylene. This finding rules out the earlier suggestions by the same authors, that so called "λ 4050 group", observed in spectra of comets is due to methylene[17]. The full report on the methylene spectrum including new features found in the visible and ultra-violet regions was given by Herzberg a year later[102].

Out of all reactions producing methylene mentioned above, two are utilized as sources to study its reactions, namely the photodecompositions of keten and diazomethane. Therefore we will consider these reactions in more detail.

The complexity of the photolyses when keten or diazomethane are the sole components of the photolysed mixture is caused by secondary reactions, following the primary act of splitting the molecule into two fragments. Much work has been done to elucidate the mechanism of these reactions[19-25];

the most probable sequence of the reaction of keten at ordinary intensities of light is:

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad (a)$$

$$CH_2 + CO \longrightarrow CH_2CO^* \qquad (1)$$

$$CH_2 + CH_2CO \longrightarrow C_2H_4 + CO \qquad (2)$$

$$CH_2 + CH_2CO \longrightarrow (CH_2)_2CO \qquad (3)$$

$$CH_2 + C_2H_4 \longrightarrow C_3H_6 \qquad (4)$$

$$(CH_2)_2CO + CH_2CO \longrightarrow (CH_2)_3CO + CO \qquad (5)$$

$$CH_2CO + M \longrightarrow CH_2CO + M \qquad (6)$$

$$CH_2CO^* \longrightarrow CH_2 + CO \qquad (7)$$

Further reactions of type (4) and (5) could account for the formation of products of higher molecular weight, found deposited on the walls of the reaction vessel, and could also explain the fact that the ratio $\frac{CO}{C_2H_4}$ was found to be larger than 2. Ethylene is formed only by reaction (2), - no direct association of two methylenes occurs.

At higher intensities of light which occur in flash photolysis new possibilities arise due to the adiabatic heating[20]. The formation of additional products in this case CH_4, C_2H_2, H_2, C_2H_6 and carbon is explicable on the grounds of new reactions such as disproportionation of CH_2 : $2CH_2 \longrightarrow CH_3 +$ which is followed by the chain reactions of formed radicals.

Similar products were found in the thermal decomposition of diazomethane[26] at temperatures higher than 500°C which proved that their formation is related to reactions of CH_2 itself rather than to the reactions of keten with methylene.

Another factor affecting the mechanism of photolysis of keten besides the light-intensity is the frequency of radiation. The long wavelength limit

for this photolysis lies between 3700-3900 Å. At these wavelengths however the quantum yield is low and pressure-dependent, implying that excited keten molecules are produced predominantly. At lower wavelengths, in the region 3100-2700 Å the quantum yield equals 1; every quantum absorbed brings about the decomposition.

Photolysis of diazomethane, producing ethylene, propylene, nitrogen and a non-volatile liquid (probably a pyrazoline derivative) is described by the following scheme:

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2 \qquad (1)$$

$$CH_2 + CH_2N_2 \longrightarrow C_2H_4 + N_2 \qquad (2)$$

$$C_2H_4 + CH_2 \longrightarrow C_3H_6 \qquad (3)$$

$$C_2H_4 + CH_2N_2 \longrightarrow C_3H_6N_2$$
$$C_3H_6 + CH_2N_2 \longrightarrow C_4H_8N_2 \qquad (4)$$

The last two reactions were suggested to explain the high quantum yield of 4, not accompanied evidently by a chain reaction, and also a formation of a higher boiling residue containing nitrogen.

The secondary reactions in the photolyses of keten and diazomethane can be avoided in studied of reactions of methylene with other compounds, by maintaining a low concentration of a methylene-source compared with a concentration of the other reactant - thus preventing methylene from reacting with its precursors before it reacts with the appropriate molecule.

The life-time of methylene varies, as it was pointed out by Norrish[27], with the conditions of experiments and the source. Pearson[9] reports values of 5×10^{-3} sec. and > 1 sec. for lifetimes of methylene in diazomethane and keten respectively. The main factor influence $\lambda_{1/2}$ is concentration.

Addition of only 2 mm. of N_2 for example extended the former value to 250×10^{-3} sec. Norrish[27] found that under the same experimental conditions $\lambda_{1/2}$'s of methylene from keten, and methyl from acetone were of the same order of magnitude, and that both values would be altered within wide limits by changing the pressure and flow rate. Herzberg[16] gives the value of 15 μsec. at 002 mm. of diazomethane and 2 mm. of nitrogen, which corresponds to the rate of collisions between methylene and diazomethane.

What seems to be established from these experiments is the fact that $\lambda_{1/2}$ of methylene from diazomethane is bigger than that from keten, or in other words the former species are more reactive than the latter. This finding is supported by the results of reactions of methylene from these two sources as we shall see in the next paragraph.

1.2 TYPES OF REACTIONS

a) Insertion reactions

In this type of reaction methylene interposes between two neighbouring atoms of the attacked compound producing the next higher homologue.
The most extensive studies on this type of conversion have been done on insertion of methylene into C-H bonds.
The pioneering, mostly qualitative work in this field was carried out in 1942 by Meerwein et al[28] who, examining the photolysis of diazomethane in solutions of some ethers and alcohols, observed the formation of their higher homologues. Since then, most of the work has been done with hydrocarbons. In the simplest paraffin-methane, attack of methylene on a molecule produces ethane[29] according to the reaction:

$$CH_2 + CH_4 \longrightarrow C_2H_6$$

Higher hydrocarbons beginning with propane yield a mixture of isomers due to the concurrent attack of methylene on various bonds. Thus the reaction with propane produces n-butane and isobutane from the insertion into primary and secondary C-H bonds respectively[30,31].
In all known cases the insertion occurs at a C-H bond. The possibility of formation of higher hydrocarbons by insertion into C-C bonds was ruled out on the grounds, that no extension of the ring was observed when methylene reacted with cyclopropane,[31,32,33] cyclopentane[34] and tetrahydrofuran[35]. The sole products of above reactions were methyl-derivatives of the cyclic compounds.

These general qualitative conclusions seem to hold for various sources of methylene and various conditions of the reaction. Differences arise when one tries to estimate quantitatively the relative rates of attack

of methylene on various C-H bonds of hydrocarbons in different media. Thus Doering and Buttery[34], photolysing diazomethane in solution of hydrocarbons, found the statistical distribution of products resulting from insertion from insertion into C-H bonds, which corresponded to equal rates of attack on these bonds; methylene failed to distinguish not only between primary, secondary and tertiary C-H bonds, but even between these and allylic or vinyl types.

Random reactivity of methylene from diazomethane with hydrocarbons in solution was confirmed by Richardson et al[36] in studies on C_7, C_8, C_9 alkanes.

Utilising the same source of methylene, but working in the gas phase Frey[37] found discrimination in the reaction with primary, secondary, tertiary C-H bonds, in alkanes, the order of the rates of attack being

$$k_{primary} \underset{1.0}{=} > k_{secondary} \underset{1.2}{=} > k_{tertiary} \underset{1.5}{=}$$

The discrimination increases further when one employs keten as a precursor of methylene.[30,31]

Similarly, in the case of olefins one can observe the discrimination in insertion into C-H bonds. Table 1.1 gives the rates of attack of methylene on a wide range of C-H bonds relative to the rate of attack on the double bond of olefins, taking into account the number of bonds of the given type in each compound, and the experimental conditions (source of methylene, wavelength of employed radiation).

TABLE 1.1.

Substrate	Conditions of experiments	Rates of attack on bonds: C = C	H C-H 1 H	H 1 -C- 1 H	-C = C(H)H	-C = C(H)	Ref.
Ethylene	CH_2CO - 3100 Å	1			0.11		31
Propylene	CH_2CO - 3100 Å	1	0.06		0.035	0.024	41
	CH_2N_2 - polychr.	1	0.11		0.09	0.09	
Isobutene	CH_2CO - 3100 Å	1	0.053		0.062		42
	CH_2CO - polychr.	1	0.051		0.056		
	CH_2N_2 - polychr.	1	0.10		0.09		
	CH_2N_2 + inert gas	1	0.051		0.059		
Butene-1	CH_2CO - polychr.	1	0.07	0.09	0.05	0.04	this work
	$CH_2CO + N_2$ -"-	1	0.05	0.07	0.04	0.02	
	$CH_2CO + O_2$ -"-	1	0.10	0.11	0.06	0.03	
Pentene-1	CH_2CO - polychr.	1	0.09	0.11	0.04	0.04	this work
	CH_2CO quartz						
	CH_2N_2 polychr.	1	0.13	0.13	0.09	0.05+2	
Butadiene	CH_2CO - polychr.	1	-	-	0.06	0.047	this work
	CH_2N_2 - polychr.	1	-	-	0.085	0.077	

The correlation between the type of a bond and the rate of attack of methylene on it is the same throughout the series: namely the weaker bonds are attacked faster than the stronger ones, the sequence of the rates being:

$$k_{sec.} > k_{prim.} > \begin{matrix} k \\ = C \end{matrix}\!\!\begin{matrix} H \\ \diagdown \\ H \end{matrix} \gg k \begin{matrix} H \\ | \\ -C = C \end{matrix}$$

The numerical values of the rate of attack on the same bond throughout the series of hydrocarbons are almost the same (with the exception of ethylene) for the same set of experimental conditions. As the heats of reaction are very close one to the other, one could infer that activation energies are probably very similar too. The small differences in relative rates in this series could then be attributed to the different steric factors of the reactions.

The differences in rates of attach of methylene on various bonds in the same hydrocarbon summarised by the sequence given above are more evident when keten is employed as a source of methylene. In the same medium diazomethane acts in the direction of lowering energetic barriers between C-H bonds, so that they are attacked by methylene with very similar velocities, e.g., the difference in the rate of attack on the primary and secondary bonds in pentene-1 is completely destroyed, so is that between $= C\begin{matrix} H \\ \diagdown \\ H \end{matrix}$ and $= \begin{matrix} H \\ | \\ C- \end{matrix}$ bonds in butadiene, when diazomethane is used as a methylene source. Methylene from this source is less selective even in relation to the C = C bond, which is shown by the higher rates of attack on C-H bonds.

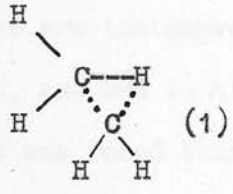
These facts corroborate the finding of the shorter lifetime of methylene from diazomethane and suggest that methylene from this source is more energetic than that from keten. The deactivating effect of inert gases however restores selectivity and values of rates of reaction with diazomethane in the presence

of inert gases are very close to those of keten.

Methylene from keten also contains some excess energy, as can be seen from some data of this work: addition of inert gases to the mixture butene-1-keten alters the rates in the direction of increase of discrimination. The exception to this rule is oxygen, addition of which seems to have an opposite effect, decreasing selectivity. The effect seems to be beyond the limits of experimental error and would suggest that other processes besides mere deactivation are taking place in this case. As we shall see later, methylene in the presence of inert gases is probably a mixture of two kinds of species in different electronic states; oxygen, being itself paramagnetic, could react selectively with one kind, leaving the other kind to the disposition of the hydrocarbons. The nature of these species will be considered in more detail in the section "Structure of methylene".

As the rates of the insertion reactions are not much affected by the wavelength of the actinic light, decomposing keten or diazomethane, and simple calculations showed that only two collisions are necessary to deactivate methylene from diazomethane one can conclude that most of the excess energy is translational.

Mechanism of insertion into C-H bonds Two alternative reaction paths have been proposed for transformation of C-H bonds into C-CH_3. In the first one the reaction proceeds via direct insertion - the transition state may be represented as follows:



(1)

(___ - the bond to be broken)
(... - the bonds to be formed)

This form of the activated complex is probably oversimplified, as is indicated by discrepancies between the experimental A factors and those calculated on this model[30,38], however it is satisfactory for the qualitative representation of the reaction scheme.

The second route assumes abstraction of hydrogen by methylene as the primary step, forming $CH_3^{\cdot}$ and alkyl radicals, which can subsequently combine to give the reaction products, according to the scheme:

$$CH_2 + R\text{-}\overset{\displaystyle H}{\overset{|}{C}}\text{-}H \longrightarrow CH_3^{\cdot} + R\text{-}\overset{\displaystyle H}{\overset{|}{C}}{}^{\cdot} \qquad (2)$$

$$CH_3^{\cdot} + R\text{-}\overset{\displaystyle H}{\overset{|}{C}}{}^{\cdot} \longrightarrow R\text{-}\overset{\displaystyle H}{\overset{|}{C}}\text{-}CH_3$$

The occurrence of the latter mechanism was confirmed by the existence of some products of CH_3 and alkyl-radical reactions in the reactions of methylene[39]. These products diminished in the presence of radical-scavengers such as oxygen or NO.

Probably both routes contribute to the general scheme of the reaction. Doering and Prinzbach[40] made some attempts to estimate the proportion of the reaction going through routes (1) and (2), by using the C^{14} labelled hydrocarbons. They found it to be 5:2:1. This figure is consistent with Frey's results which give value ~ 20% for the radical component of the reaction.

Insertion of methylene into bonds other than C-H is known only in a few instances: these are the conversions of C-Cl, C-Br bonds into $C\text{-}CH_2Cl$, $C\text{-}CH_2Br$ respectively, and O-H in alcohols into $O\text{-}CH_3$.

In the first case it was found that the main product formed in the photolysis of diazomethane in solution of organic halides was that derived from

interposing methylene between C and Hal. atoms[43]. The attack of methylene on the C-Cl bond in isopropyl chloride for example was found to proceed 6 times faster than the corresponding attack on the primary C-H bonds. This preference for the C-Hal bond compared with the C-H bond is probably due to the electrophilic character of methylene, and hence its attraction for halogen.
Another example of insertion in the C-Cl bond is the reaction of methylene from keten with methylene chloride, producing CH_2CHCl_2 from insertion into the C-H bond, as well as $CH_2Cl.CH_2Cl$ from insertion into the C-Cl bond. The preliminary experiments showed that the relative yields of products are pressure dependent; $CH_2Cl.CH_2Cl$ formation being favoured at higher pressures.[113]

Our knowledge of the transformation of an O-H bond into an $O-CH_3$ is confined to Meerwein's[44] finding of isopropyl-methyl ether in products of the photolysis of diazomethane in isopropyl alcohol solution, and reports on the formation of dimethyl ether from keten and methanol in the gas phase[45]. The ratio of yields of products $-\frac{(\text{ethanol})}{(\text{dimethyl ether})}$ - in the latter case suggested equal rates of attack of methylene on C-H and O-H bonds in methanol.

Failure to detect N-methylpiperidine in the reaction of N-methyl pyrolidine with diazomethane implies that the insertion into the C-N bond does not take place.
Similarly Franzen's[112] experiments with $^{14}CH_2$ and diethyl ether in which all ^{14}C in ethyl-propyl ether was detected in the γ position ($CH_3-CH_2-O-CH_2-CH_2-^{14}CH_3$) - suggest that methylene does not react with the C-O bond either. (If such a reaction took place one would have obtained some ethyl-propyl ether with ^{14}C in the γ position.)

b) ABSTRACTION AND DISPLACEMENT REACTIONS

In contradistinction to insertion and addition reactions, where methylene simply attaches itself to the attacked molecule, the displacement and abstraction reactions result in elimination of a fragment of this molecule by methylene.

In the former case methylene displaces an olefin - the residual part of the reacting compound forms the lower homologue e.g.:

$$CH_2 + C_2H_5\text{-}O\text{-}C_2H_5 \rightarrow C_2H_4 + CH_3\text{-}O\text{-}C_2H_5$$

Both products formed in this reaction are stable compounds.

In the latter case both the eliminated and residual fragments are radicals, which can subsequently undergo various transformations, frequently leading to a chain reaction. For instance the abstraction of a hydrogen atom from alkanes leads to the formation of CH_3 and alkyl radicals, which can combine, disproportionate or abstract another hydrogen.

The only displacement reaction of methylene known so far is one with ethers[46]. It was shown that when methylene generated from keten reacted in the gas phase with diethyl, ethyl- propyl and di-isopropyl ethers, ethylene, ethylene + propylene and propylene respectively were found as the reaction products, together with the lower ethers. The scheme of the reaction may be pictured as follows:

$$CH_2 + C_2H_5\text{-}O\text{-}C_2H_5 \rightarrow CH_3\text{-}O\text{-}C_2H_5 + C_2H_4$$
$$CH_2 + C_2H_5\text{-}O\text{-}C_3H_7 \rightarrow CH_3\text{-}O\text{-}C_3H_7 + C_2H_4$$
$$\rightarrow CH_3\text{-}O\text{-}C_2H_5 + C_3H_6$$
$$CH_2 + (iso\text{-}C_3H_7)_2O \rightarrow CH_3\text{-}O\text{-}isoC_3H_7 + C_3H_6$$

The elimination of the defin from the ethyl group was favoured over the analogous process with the iso propyl group which is understandable in view of the larger steric hindrance in the latter group. The temperature coefficients of the reactions were found to be very small.

The simplest case of the methylene abstraction reaction would be an abstraction of a hydrogen atom from a hydrogen molecule:

$$CH_2 + H_2 \longrightarrow CH_3^{\cdot} + H \qquad (1)$$

Several workers[47;50] have examined the reaction of methylene with molecular hydrogen. Although there are discrepancies in the formation of CH_4, C_2H_6 and higher hydrocarbons in this reaction amongst various authors, the general conclusion seems to be that reaction (1) followed by:

$$CH_2CO + H \longrightarrow CH_3^{\cdot} + CO$$
$$2CH_3^{\cdot} \longrightarrow C_2H_6$$
$$CH_3^{\cdot} + H_2 \longrightarrow CH_4 + H$$

is of importance only at higher temperatures $> 100^{\circ}C$. The activation energy for the reaction (1) is according to Steacie[49] less than 2 kcal, the A factor is equal 10^{10} $mole^{-1}l$ sec^{-1}. At low temperatures however the direct association $CH_2 + H_2 \rightarrow CH_4$ takes place.

Another example of hydrogen abstraction by methylene is supplied by the presence of "the radical component" in the insertion reaction, mentioned in the previous paragraph. The formation of the CH_3 and alkyl radicals in this reaction is explained by the abstraction of the hydrogen atom from the hydrocarbon. In the case of propane, two radicals are produced as the result

of abstraction from the primary and secondary C-H bonds:

$$CH_2 + CH_3-CH_2-CH_3 \rightarrow CH_3^{\cdot} + {}^{\cdot}CH_2-CH_2-CH_3$$
$$\rightarrow CH_3^{\cdot} + CH_3-\dot{C}H-CH_3$$

The abstraction from the secondary one is 7 times faster than that from the primary[39]. In this aspect methylene resembles methyl. This reaction is not only confined to alkanes: abstraction of the hydrogen atom from allene for instance yields the $CH\equiv C-CH_2^{\cdot}$ radical, which combines with $CH_3^{\cdot}$ giving ethylacetylene[51]. Similarly the presence of aldehydes in the reaction of methylene with ethers[46] was explained by the abstraction from the ether followed by the decomposition of the radical formed:

$$CH_2 + C_2H_5-O-C_2H_5 \rightarrow CH_3^{\cdot} + CH_3-CH-O-C_2H_5$$
$$CH_3\dot{C}HOC_2H_5 \rightarrow CH_3CHO + C_2H_5^{\cdot}$$

In the case of isopropyl ether this reaction produces acetone and the isopropyl radical; the abstraction from the tertiary C-H bond was found to be faster than that from the secondary, with a difference in activation energies of ~ 4 kcal.

The only abstraction by methylene of an atom other than hydrogen is the rather hypothetical abstraction of chlorine in the reaction of CCl_4 with diazomethane. To account for the formation of the product in which four molecules of CH_2 are attached to one molecule of CCl_4, of the form $C(CH_2Cl)_4$, a chain mechanism initiated by Cl-abstraction was postulated. The first steps of the reaction may be envisaged as shown below:

$$CH_2 + CCl_4 \rightarrow \dot{C}H_2Cl + \dot{C}Cl_3 \qquad (1)$$

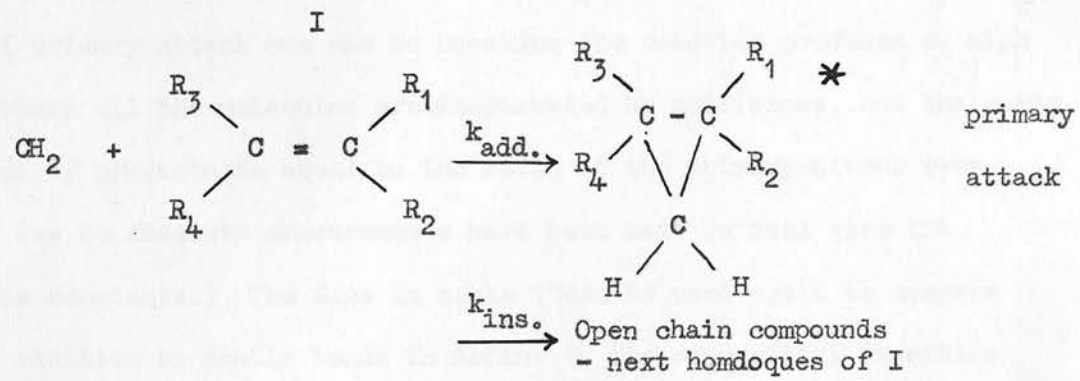
$$\dot{C}Cl_3 + CH_2N_2 \rightarrow Cl_3CCH_2 + N_2 \qquad (2)$$

$$\dot{C}Cl_3CH_2 \rightarrow \dot{C}Cl_2CH_2Cl \qquad (3)$$

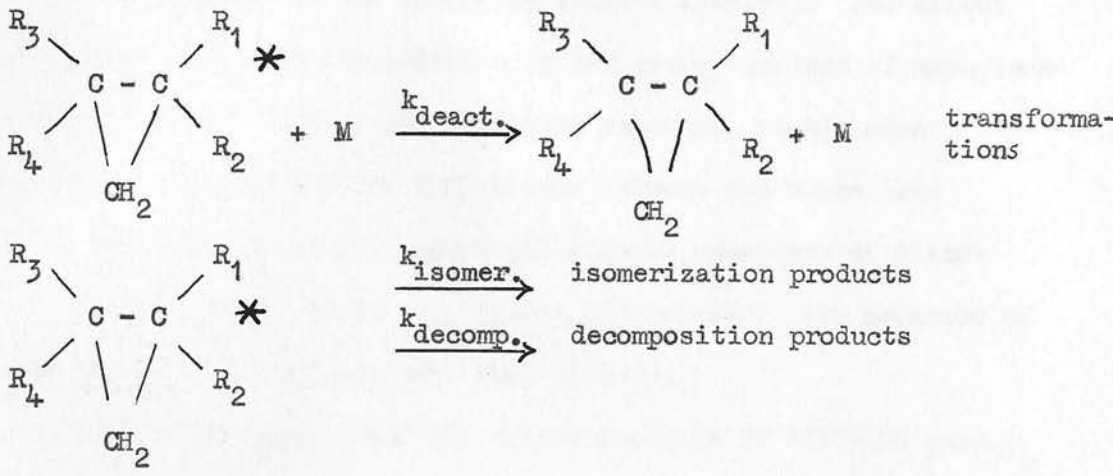
Further reactions with diazomethane of the type (2) following the rearrangement (3) would lead in the end to the compound obtained experimentally.

c) ADDITION REACTIONS OF METHYLENE

The extensive studies on the reactions of methylene with olefins indicate that methylene adds across the double bond producing a cyclopropane derivative. The simplest, olefin-ethylene forms cyclopropane itself[31,32,53,54]. The exothermicity of the reaction, together with the excess energy which the methylene species is carrying, result in vibrational excitation of the products, so that they are able to undergo further transformations such as structural and geometrical isomerizations or decomposition, unless stabilized by collisions. Concurrently with the addition to the double bond, the insertion of methylene into the C-H bonds of olefins takes place, so that the general scheme of the reaction may be represented as:



followed by:



where - R_1, R_2, R_3, R_4 are H -atoms, or any alkyl group.

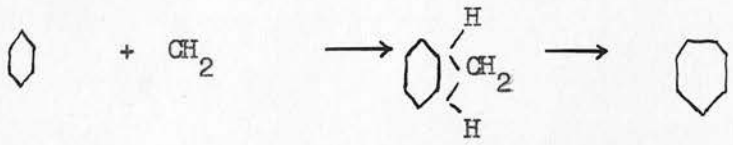
The second part of the reaction received much consideration in view of its applications to the theory of unimolecular reactions and intra-and intermolecular energy transfer. Accumulation of the evidence concerning this subject in recent years requires more detailed review, so for the sake of clarity we shall deal with this problem separately, attempting to describe only the primary attack of methylene on the double bond in the present chapter.

In accord with the above scheme the distribution of the products varies with the pressure of the system. In order to get the information about the rates of primary attack one has to consider the reaction products at high pressures, where all the molecules are deactivated by collisions, and the ratio of the yields of products is equal to the ratio of the primary-attack rate constants. (as no absolute measurements have been made we deal with the relative rate constants.) The data in table 1 can be used again to compare the rate of addition to double bonds in defins to the concomitant insertion into the C-H bonds. As can be seen from the above table methylene attacks the double bond overwhelmingly faster than the C-H bond (~20 times faster for the

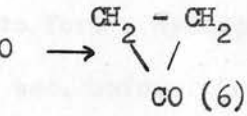
methylene from keten, closest to the thermally neutral species). The effect exerted on the relative rate of the addition by the energy content of methylene shows an analogous trend to that in the insertion reaction, namely more energetic methylene tends to make the differences between the bonds less important. This results in a lower rate of addition in reactions of diazomethane compared with those of keten by a factor of ~1.5-2.0. The presence of inert gases restores the discrimination to that of keten.

The structure of defins does not affect the rate of addition much. There is a slight difference between the defins and dienes, as can be seen from the data on butene-1 and butadiene from this work. The conjugated system lowers the rate of the addition a little compared to the insertion into vinyl C-H bonds. The only other case of addition to the double bond studied quantitatively is, reported in this work, addition to the double bond of tetrafluoroethylene. It was found that no insertion into the C-F bond occurs; methylene only adds to the double bond to form tetrafluorocyclopropane.

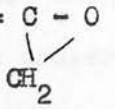
Other cases of the methylene addition to the double bond studied qualitatively include addition to aromatics, producing in the reaction of diazomethane with benzene[54,55] norcaradiene, which isomerizes to cycloheptatriene:



and addition of methylene to keten[19], or CO_2[56]. The last two reactions are rather hypothetical, postulated as intermediate steps in formation of C_2H_4 in the photolysis of keten in the gas phase (1), and formaldehyde in the reaction of keten with CO_2 (2).

(1) $CH_2 + CH_2 = CO \longrightarrow$  $\longrightarrow C_2H_4 + CO$

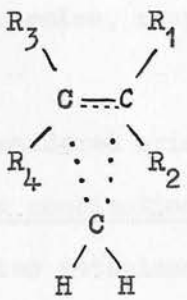
CO (6)

(2) $CH_2 + O = C = O \longrightarrow$  $\longrightarrow HCHO + CO$

Although cyclopropanone (6) has not been isolated in the gas phase, there is evidence for its existence in solution[57], which makes the mechanism (1) quite plausible.

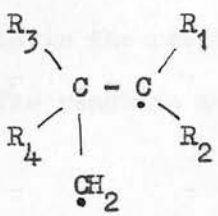
Mechanism of addition to the double bond: By analogy with the non-radical and radical routes of insertion into the C-H bond one can postulate two ways in which methylene adds to a double bond.

The first one resembles the three centre addition, in which the CH_2 molecule is joined simultaneously to both carbon atoms of the C=C link, the activated complex being:



(---- bond to be broken)
(.... bonds to be formed)

In the second route the first step is the formation of an intermediate biradical of the trimethylene form;



which can subsequently cyclize to form a cyclopropane ring. Internal rotation with the velocity $10^{-10} - 10^{-13}$ sec. before the cyclization takes place, can lead to nonstereospecificity in addition. The first scheme, where no such open intermediate exists would imply the conservation of stereospecificity. Experimental data on addition of methylene to cis- and trans-butene-2[58,59], support the former mechanism on the grounds that the above reactions yield only pure cis- or trans-1,2 dimethylcyclopropanes respectively, provided the pressure in the experiments is high enough to prevent the geometrical isomerization /cis → trans/ which obscures the interpretation of the results at lower pressures.

In some experiments however carried out with a great excess of inert gas it was found that stereospecificity was lost[60,61]. Explanation of this fact demands some information about the structure of methylene, so we shall leave this problem open till the appropriate section, confining the present considerations to the statement that methylene under various conditions may contain two different kinds of species, responsible for the radical and non-radical behaviours.

Having considered briefly all the main types of the methylene reactions we must consider the combination reaction.

The combination of two methylenes to give the ethylene molecule is doubtful as it was shown that the latter is formed by the faster process of abstraction of the methylene group from diazomethane or keten. The only combination known so far is the reaction of methylene with CO[62,63], producing keten. The mechanism of the reaction was established by the experiments with ^{14}CO, as it was found that keten regenerated in the reaction of the ordinary keten with ^{14}CO contained some ^{14}C. The reaction scheme can be thus described as follows:

$$CH_2CO \longrightarrow CH_2 + CO$$

$$CH_2 + {}^{14}CO \longrightarrow CH_2{}^{14}CO$$

1.3 STRUCTURE OF METHYLENE

The structure of methylene, particularly its ground state has been a subject of much speculation in recent years.

It has been frequently considered on theoretical grounds that methylene may be envisaged as the simplest organic entity with the properties of a physically and chemically stable molecule, arising from divalent ^3P carbon. If this is the case, pure p orbitals of the carbon atom would be employed in the formation of the CH_2 molecule, and the H-C-H angle should be a right angle, (neglecting repulsion between the hydrogen atoms, which increases it) and the molecule would be in the singlet state.

On the other hand the high reactivity of methylene would indicate a radical character, i.e., the presence of unpaired electrons. This is only feasible if some hybridization of the carbon electrons takes place. Assuming this hybrid to have a digonal sp form we must postulate the linear structure for methylene, and bearing in mind the principle of maximum multiplicity - the triplet for its electronic state.

Early, rather naive experiments with nitric oxide[64] undertaken with the prospect of proving the radical nature of methylene did not appear to be significant; the small extent of the $CH_2 + NO \longrightarrow CH_2NO$ reaction could be explained by assumption, that the reverse decomposition of CH_2NO takes place. In the light of the fact that CH_2NO is a radical itself, this assumption seems to be quite plausible.

Herzberg[102] ascribed two absorption systems found in the spectrum of methylene (one with a linear configuration in the lower state, the other bent) to two modifications of methylene of different multiplicity. The

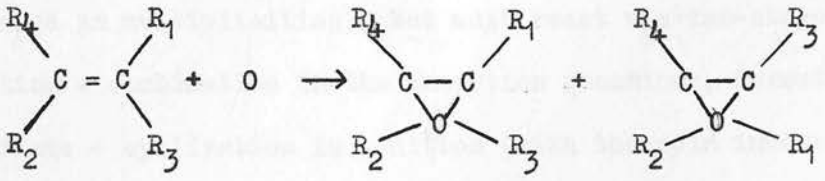
The magnitude of the energy difference between the two states is not known, however his conclusion that the ground state of methylene is the linear triplet seems to be certain.

The newly formed methylene, however, need not be in the ground state. Accumulation of evidence about the reactions of methylene in recent years provides some information about its configuration when the nearly formed methylene reacts with other compounds. This is a rather unique case, contradicting the general belief that knowledge of the kinetics and mechanism of the reaction does not provide information about the electronic structure of reacting species.

Thus Skell etal[65] inferred on a semi-intuitive basis that the stereospecificity in the addition of methylene to defins indicated the singlet state. The triplet state of methylene would imply formation of the biradical (see 1.2C) with two unpaired electrons as the primary step; internal rotation before the spin inversion and cyclization occurs, would lead to the nonstereospecific addition.

The singlet methylene would be capable only of simultaneous addition to the double bond.

Nonstereospecificity as the criterion of the triplet state is supported by the addition of atomic oxygen to olefins[66]: from the cis-olefin one gets both cis and trans epoxycompounds according to the scheme:



We have mentioned in the preceding chapter that the addition of methylene has the stereospecific character. However in a large excess of inert gas this stereospecificity was lost[60,61].

This finding can be explained in terms of the following scheme: (a) methylene when formed, photolytically, or thermally[67] is in the excited-singlet state (stereospecificity is maintained); (b) collisions with inert gas degrade excited singlet species to the state, which in view of the loss of stereospecificity is a triplet.

The conclusion that newly formed methylene is in a promoted state is consistent with early observations by Bawn and Dawning[15], who found that the D-line of sodium was emitted when it reacted with methylene-halides; the deficit of energy equal to the difference between the energy of the D-line light quantum and the exothermicity of the reaction could be supplied by a transition of methylene formed in this reaction to the lower energetic state.

That explanation could also partially account for the increase in selectivity of methylene towards C-H bonds in the presence of inert gas, if we assume that triplet methylene present under these conditions reacts like a radical and is discriminative. (The twofold effect of inert gas on methylene, reducing translational energy as well as electronic, does not permit us to estimate the extent of the singlet-triplet transition.)

Generally we could attempt to attribute "the radical component of the methylene reactions[11] to the triplet species, which are unable to attach to two atoms of the attacked bond simultaneously (this would involve the one-step change in multiplicities), but must react via two-stage routes: abstraction + combination in the insertion reactions, formation of an open intermediate + cyclization in addition (with the spin inversion between the two stages).

It is also conceivable that the reduced selectivity of methylene in the presence of oxygen is due to triplet methylene reacting readily with the oxygen, which has like multiplicity so that the singlet species left reacts less selectively.

The only case of the pure triplet methylene reported so far comes from the photosensitized decomposition of diazomethane with benzophenone as photosensitizer.[68]
The authors believe that benzophenone in the triplet state forms the triplet diazomethane in collisions, which decomposes subsequently into triplet methylene and nitrogen.

It is interesting to compare methylene with some of the other carbenes.
Addition of dichloro- and dibromocarbenes to defins[69,70] studied in solution showed stereospecificity anticipated for the singlet species. Similarly difluorocarbene and carbethoxycarbene are probably in the singlet - non radical state. Diphenylmethylene on the other hand adds to defins via the biradical path, and also reacts readily with oxygen forming benzophenone[65,72]. This behaviour indicates triplet as its electronic state.

1.4 APPLICATIONS OF THE METHYLENE ADDITION REACTIONS TO STUDIES OF UNIMOLECULAR REACTIONS

When methylene adds to the double bond of an olefin, the heat of the reaction, together with the excess energy carried over by methylene, results in the formation of vibrationally excited cyclopropane derivative, capable of further re-arrangement.

Studies of the reactions of the "hot" molecules formed in this way with a definite energy content, supplemented by the concurrent investigations of thermal decompositions offer means of proving the validity of various theories of unimolecular reactions, and the related subject of intramolecular energy transfer.

Two theories of unimolecular reactions have been proposed in recent years; the one connected with the name of Slater, the second with those of Hinshelwood, Rice, Ramsperger and Kassel (for the sake of brevity we shall call the latter as it is generally accepted the R.R.K. - theory). Both of them explain the high pressures values of rate constants, both assume that the rate constant depends on the total energy content of the reacting molecule according to the equation:

$$k = \nu \left(\frac{E-E_o}{E}\right)^{n-1} \qquad (1)$$

where: E = total energy of the reacting molecules
E_o = activation energy of the process
ν = constant equal to k of molecules of very high energy
n = adjustable parameter dependent on the number of degrees of freedom of the molecule to the first approximation

The discrepancy between the theories appears at the low pressure value of the rate constant and is brought about by different assumptions about the conditions of energization of the molecule. Thus Slater assumes

no redistribution of energy gained in collisions amongst the modes of vibration in the molecule, during the period of vibration, whereas the R.R.K. theory allows energy to flow freely between the normal modes of vibration. Difficulty in finding a suitable reaction is the reason why only a few cases are known to which these theories were applied. (A survey of these cases is given by Gill and Laidler[73], and Laidler and Wojciechowski[104] who also attempt to reconcile the R.R.K. (and Slater's theories).)

One of the first cases to which the Slater's theory was applied successfully was the thermal isomerization of cyclopropane; agreement between the calculated fall-off curve[74] and the experimental one obtained by Pritchard, Bowden and Trotman-Dickenson[75] was very good. Studies of the higher cyclopropanes are less ambitious due to the lack of the vibrational analysis: one cannot directly apply the theoretical formulae in these cases, however this system enables us to investigate in a semi-quantitative way the following aspects of unimolecular reactions:

(1) The effect of substituents, or generally speaking the effect of increasing the number of degrees of freedom on rate constants of isomerization,

(2) The effect of different energy contents of reacting molecules on the rate-constant of isomerization: we can produce the cyclopropane derivatives thermally excited, or chemically excited by the addition of methylene of different energy content to defins,

(3) The existence, or non-existence of the energy flow in the molecule, from the distribution of products formed from the species in different states of vibrational excitation.

Table 1.2 summarises the data on isomerization of a number of cyclopropane derivatives, formed in the methylene addition reaction.

The second column in this table describes the way in which the excited molecule is formed: the parent olefin, the methylene source and wavelength of the radiation used.

Values of the activation energy for each decomposition - E_δ are obtained from the thermal decomposition data, given in references cited in the last column of the table.

The ratio $\frac{k_{isom}}{k_{deact}}$ given in the fourth column is taken as a measure of k_{isom} (assuming k_{deact} to be the same throughout the whole series of compounds).

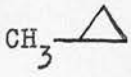
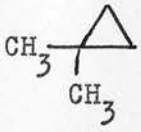
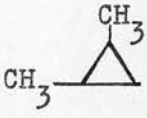
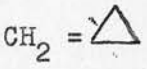
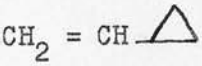
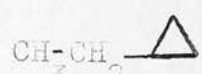
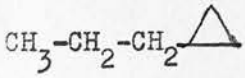
The values of this ratio are obtained from the plot of the ratio $\frac{\text{yield of straight chain products}}{\text{yield of cyclopropane derivative}}$ vs the reciprocal of pressure. Steady state equation applied to the reaction scheme (see p. 17 and 18) yields:

$$\frac{(\text{straight chain products})}{(\text{cyclopropane derivative})} = \frac{k_{ins}}{k_{add}} + \frac{k_{isom}}{k_{deact}[M]} \times \left(1 + \frac{k_{ins}}{k_{add}}\right)$$

Hence $\frac{k_{isom}}{k_{deact}}$ is the slope of the above-mentioned plot. The values of $\frac{k_{isom}}{k_{deact}}$ were calculated when necessary from the data given in the appropriate references.

We shall discuss now the various aspects of unimolecular reactions in the light of experimental data of table 1.2.

Table 1.2

Molecule	Source of Molecule	E_o (kcal/mole)	$\frac{k_{isomerization}}{k_{deactivation}}$ (atm.)	References
	CH_2CO + ethylene	65	1.19	31, 76,75,77,103
	CH_2CO + △ (2600A)		0.202	41,
	CH_2CO + △ (3100A)		0.284	
	CH_2N_2 + △ (polychr.)		0.437	
	CH_2CO + propylene (2600A)	65	0.041	78,
	CH_2CO + propylene (3100A)		0.060	
	CH_2N_2 + propylene (pol.)		0.120	
	CH_2CO + isobutene (p.)		0.0032	79,80,
	CH_2N_2 + isobutene (p.)		0.020 ± 0.005	42,
		62.5		81,
	CH_2N_2 + transbutene-2 (4358A)	59.5 (geom. isom)	0.020 ± 0.001	59, 82,
		62 (struct. isom)		83,
	CH_2CO + allene (p.) (4538A)		0.22	51,
	CH_2N_2 + allene (3660A)		0.47 0.67	
	CH_2CO + butadiene (p.)		0.026	This work
	CH_2N_2 + butadiene (p.)	49.6 (isomerization to cyclopentene)	0.123	84,
	CH_2CO + butene-1		Unmeasurable	This work
	CH_2N_2 + butene-1	64	0.004 ± 0.001	85,
	CH_2CO + pentene-1		0	This work
	CH_2N_2 + pentene-1			

Firstly: in order to compare the effect of the additional number of degrees of freedom on the rate constants of the unimolecular process, the activation energy E_0 should remain constant throughout the series of reactions. This condition, as can be seen from the table 1.2, is satisfied for cyclopropane and methylcyclopropane and the difference between them and the next homoloques is small in the case of the compounds formed from methylene, compared with the total energy content. The differences in the values of $\frac{k_{isom}}{k_{deact}}$ for the series of the cyclopropane derivatives, formed from the same source of methylene, can be thus attributed to the different number of modes of vibration in these coumpounds.

The change of 21 degrees of freedom in cyclopropane to 30 in methylcyclopropane brings about a 20-fold decrease in the rate of isomerization. Dimethylcycloporpanes isomerise slower than methylcyclopropane, no isomerization of propylcyclopropane formed from pentene-1 and keten was observed down to the pressure of ~ 5 mm.

The general trend is verified experimentally that the more complicated the molecule, i.e., more degrees of freedom between which the energy can be distributed, the longer the life-time of the molecule, i.e., the smaller the rate constant of isomerization is.

It is well known that only some of the vibrational degrees of freedom contribute to the actual reaction (13 out of 21 for cyclopropane, 19 out of 30 for methylcyclopropane); "n" in the equation (1) represents the number of these effective ones, which depends on the structure of the molecule and its symmetry.

Comparison of the rate of isomerization of C_5H_{11}-cyclopropanes; 1,1 and 1,2 dimethylcyclopropanes and ethylcyclopropane can provide the information about the effect of structural factors on "n". The situation is a bit obscured by the fact that 1,2 dimethylcyclopropane undergoes not only a structural isomerization to various pentenes, but also the concomitant geometrical isomerization: cis 1,2 dimethylcyclopropane to the trans-compound and vice versa. The latter is faster than the former (both lower activation energy and higher A factor contribute to this).

The elucidation of accurate figures for the rate constants of these two kinds of isomerization is difficult from the known data, so the value 0.019 atm. represents the total rate constant. However, even excluding this case and taking into account 1,1 dimethyl- and ethyl-cyclopropanes which are eligible only for the structural isomerization, one is struck by the difference in the rate constants for these compounds. This difference cannot be explained by their different energy contents, as the activation energies for the thermal isomerization are almost identical and it is rather improbable that the heat of both addition reactions should differ so much, so that the 5-fold greater rate of isomerization of 1,1 dimethylcycloporpane compared to ethylcyclopropane must be ascribed to the different number of "n's". Crude estimation of the difference in n's causing the 5-fold decrease in the rate constants applying equation (1) gives a value of 1.7. The straight chain attached to the cyclopropane ring seems to lower the rate of isomerization, compared to the two single substituents.

Considering the second aspect of the reactions in question namely the effect of the different energy content on the rate of isomerization, one

observes a large difference of order of ~ 1,000 between the rates of isomerization of molecules excited thermally and by the addition of methylene, and smaller changes amongst the latter ones, depending on the conditions of their formation (wavelength, mode of addition, source of methylene). These observations are in accord with the theoretical conclusions (see equation 1), that the larger the energy content of the molecule the higher the rate constant, as in the thermal decomposition the excess energy is of order of a few kilocalories, whereas in the decomposition of the chemically excited molecules this excess amounts to ~ 30kcals.

In the first case the excess of energy corresponds to the thermal excitation of molecules at a given temperature. The estimation of the energy content in the second case is complicated by the lack of unambiguous data on the heat of reaction which contribute the largest share to the energy content.

The heat of the methylene-addition reaction is defined as;

$$\Delta H = \Delta H_{f}^{\circ} \left({}_{R}\Delta\right) - \Delta H_{f}^{\circ}(CH_2) - \Delta_{f}^{\circ}H \text{ (olefin)}$$

Except for the first case of ethylene producing cyclopropane, the heats of formation of the other cyclopropane derivatives are unknown. Assuming, however, that the difference between ΔH_{f}°s for an olefin and a cyclopropane derivative is small (which is to some extent justified by the value of 0.02 kcal. for this difference in the case of ethylene → cyclopropane) one arrives at the conclusion that the exothermicity of the addition reaction is due to the endothermicity of the formation of methylene.

Unfortunately the heat of formation of methylene has not been determined accurately, the values varying with the values of the bond dissociation energy for the CH_2-H bond in the range 67-100 kcal/mole. (A review of the most

recent literature on $D(CH_2-H)$ is given by B. E. Knox and H. B. Palmer in the article "Bond dissociation energies in small hydrocarbon molecules" - Chem. Rev. 1961[86]).

The generally accepted value for $\Delta H_f^\circ CH_2$ is 85 kcal/mole[89,92].

Other factors contributing to the excitation of the cyclopropanes in the methylene addition reactions are excitation of methylene itself, varying with the wavelength of the radiation used and the source of methylene and the thermal energy of the reactants, which at the temperature of the experiments (usually room temperature) is very small. As the activation energies for most of the cyclopropanes are in the vicinity of 65 kcal/mole, the excess of energy of the chemically activated molecules comes to ~ 30 kcals. Some attempts have been made to calculate roughly the excess of energy carried by methylene from various sources[87]. Assuming that methylene from the photolysis of keten at 3130 Å is in thermal equilibrium with its surroundings Frey obtained values of 5.5, 10.5 and 15.4 kcals for the excess energy for methylene from keten (radiation shorter than 3100 Å), and diazomethane (4,358 and 3,660 Å) respectively, applying the modified equation (1) to the experimental data of $k_{isom.}$ This difference results in a 2-5 fold increase in the values of the rate constants in the reactions of diazomethane compared with those of keten.

The fact that the methylene species generated from diazomethane is more energetic has been recognised in the earlier work on the insertion reaction, and could have been predicted from the higher long wavelength limit of dissociation for diazomethane. The experiments with inert gas indicated that part of this excess energy is translational, being lost on only a few collisions. Although no data are known about the difference in the electronic states of

methylene from keten and diazomethane, this possibility cannot be excluded. The variations in k_{isom} with the frequency of light decomposing the methylene precursors suggest that part of this excess energy is vibrational.

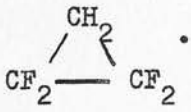
The general trend that the higher frequency radiation produces molecules of higher energy content is self-explanatory. The only exception from this is the difference between k_{isom}^{s} for methylcyclopropane produced from keten at 2,000 Å and 3,100 Å, which is opposite to this trend. It was, however, suggested that the electronic state of keten is different at these two wavelengths, which could result in the different energy contents of methylene.

Another point in comparing the thermal isomerization with the methylene addition one is the high degree of monoenergecity of the molecules in the latter case, appearing as the constancy of the $\frac{k_{isom}}{k_{deact}}$ ratio throughout the range of pressure. The small decrease in the values of rate constants at low pressures, found in the cases of 1,1 and 1,2 dimethylcyclopropanes and methylene cyclopropane formed from diazomethane and attributed to the energy spread of the methylene species from this source, was not confirmed in the work on methylcyclopropane.

Also in this work no energy spread for vinylcyclopropane was found in the experiments with diazomethane.

It was suggested by Butler and Kistiakowsky[41,88], that the secondary reactions of methylene with the products, resulting in depletion of the unsaturated butenes faster than the saturated cyclopropanes, could lead to the apparent decrease in the rate constants at low pressures. The remedy for that would be the elimination of the secondary reactions by keeping the ratio

$\frac{(\text{diazomethane})}{(\text{defin})}$ very low, which was proved in one work to be true, but could still not account for Frey's data on methylenecyclopropane and methylcyclobutane in which the curvature occurred even at a low fraction of diazomethane in the reaction mixture. The only explanation for this discrepancy would be the much longer time of irradiation, or in other words the extent of conversion in the second case, which is, due to the lack of data on this item in the appropriate papers, difficult to check. Since the preliminary experiments on the methylene reactions proved no effect of the extent of conversion on the distribution of products, it was tacitly assumed that it holds in every particular case and in the whole range of pressure, which may not be true. It should not affect a single set of experiments when usually this factor is kept constant, but would account for the discrepancies in work by various authors.

In this work for example it was found that in the reaction of C_2F_4 with keten the time of photolysis did not alter the relative yields of the products up till $\sim$ 60 minutes, but when this was exceeded the yield of the unsaturated product dropped, which is explicable by assuming a secondary reaction of methylene with it - faster than the reaction with  .

Concluding these considerations one has to admit, that the problem of the origin of the decrease in rate constants is still not solved. However, should it be the real energy spread effect, the magnitude of this is small, as in most cases where this effect was found the rate constant decreased by a factor of 0.5-1.2 over a pressure range varying by a factor of 10^3.

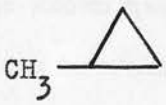
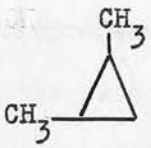
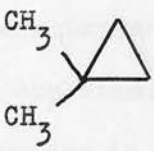
The decomposing molecules were expected to be monoenergetic from the mode of their formation.

Table 1.3 shows the change of the $\frac{k_{isom}}{k_{deact}}$ ratio with pressure for the analogous decompositions of the cyclopropane derivatives excited thermally. Values of $\frac{k_{isom}}{k_{deact}}$ were calculated from data on the change of k_{isom} with pressure, given in references 75,78,82 and 81. From the well known Lindemann mechanism;

$$1/k_{isom\ overall} = \frac{k_{activ}}{k_{isom} \times k_{deact}} + \frac{1}{k_{activ}[A]}$$

hence $\frac{k_{isom}}{k_{deact}}$ is equal to the product: slope x intercept^{-1} of the plot of $1/k_{isom\ overall}$ vs $1/A$.

Table 1.3

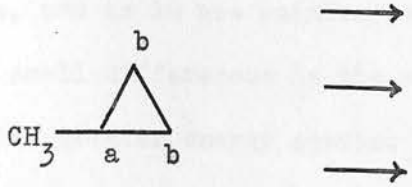
Compound	Pressure (mm Hg)	$10^4 \frac{k_{isom}}{k_{deact}}$ (atm)
	0.094	0.45
	0.120	1.14
	0.170	2.56
	0.630	10.2
	1.000	10.0
	2.080	12.7
	0.10	0.42
	0.14	0.75
	0.2	1.10
	0.3	1.9
	0.5	2.0
	1.0	2.5
	2.0	3.8
	7.0	3.4
	0.1	0.29
	0.2	0.46
	0.5	**0.90**
	1.0	1.26
	2.0	1.36
	5.0	1.30
	0.1	0.23
	0.11	0.30
	0.2	0.41
	0.5	1.1
	1.0	1.03
	2.0	1.05
	4.0	1.05

The scale of pressure is evidently different from that in the preceding case of the chemically excited molecules, but one can see that the change of pressure by the same factor as in the above case results in the change of the $\frac{k_{isom.}}{k_{deact.}}$ ratio by a factor of 5-10 (depending on the complexity of the molecule). The energy spread is then much larger in this case, which again could have been predicted from the way they became activated.

We have discussed so far the problems of unimolecular isomerization of cyclopropane derivatives without going into details of mechanism. In order to describe this we shall have to consider the distribution of products in the known cases. In addition the comparison of this distribution for various modes of formation of the same entity will provide the information about the energy flow in the given molecule.

Cyclopropane derivatives can undergo two types of isomerization: structural isomerization to the straight-chain olefins with the breaking of the cyclopropane ring and shift of the hydrogen atom, or geometrical isomerization in the case of the cyclopropane ring substituted at two carbon atoms, where this ring acts like a double bond.

The rate equations of the first type of isomerization to olefins are characterised by high values of the pre-exponential factor $\sim 10^{15}$, (that can be explained by the looser transition state due to the ring opening, i.e., the increase in eutropy[93]), and the high values of the activation energy 65 kcal. The activation energies for isomerization to various olefins are very similar. An example of this is 1-methylcyclopropane which isomerizes to isobutene, butene-1 and butene-2 depending which C-C bond in the cyclopropane ring is broken and which hydrogen migrates, according to the scheme:



$\longrightarrow$ isobutene (b-b breaks $H_a \rightarrow C_b$)

$\longrightarrow$ 1-butene (a-b breaks $H_b \rightarrow C_a$)

$\longrightarrow$ 2-butene (a-b breaks $H_b \rightarrow C_b$)

The activation energies are the same in the case of butene-1 and butene-2 and that isobutene is 2.3 kcal lower.

Such small differences in activation energies are not significant for chemically excited molecules, hence the relative rate constants of the isomerization to various products should be equal to the relative A factors of the thermal decomposition. This regularity was found to be true only to a certain extent. In the instance mentioned above it is true for the ratio $\frac{k_{\text{butene-2}}}{k_{\text{butene-1}}}$ which is the same in both thermal and photochemical decompositions of 1 methyl-cyclopropane, but shows a deviation for the $\frac{k_{\text{isobutene}}}{k_{\text{butene-1}}}$ ratio, which although twice as large in the photochemical experiments than in thermal ones, is still much lower than the ratio of A factors. (The actual value of this ratio is 0.30, whereas $\frac{A_{\text{isobutene}}}{A_{\text{butene-1}}} = 0.76$.)

Similarly the ratio of $\frac{\text{2 methyl butene-2}}{\text{3 methyl butene-1}}$ in the decomposition of 1,1 dimethylcyclopropane was found to be slightly different in the thermal and photochemical experiments, though there was no great difference in E_a's and A's for both olefins.

The last finding was once taken as proof for the non-existence of intra-molecular energy transfer[89], but was withdrawn later in the light of other

data, and as it was pointed out that these discrepancies could be still due to the small differences in the activation energies not being completely offset by the greater energy content in the chemically excited molecules. The fact that in spite of the different modes of vibration excited in the thermally and chemically activated molecules, the distribution of the products is essentially almost the same in both cases, can be regarded as proof of energy flow in the chemically excited molecule, being faster than isomerization. This is conceivable, as the vibrations in this case are mostly anharmonic and one could have expected the oscillators to be coupled, facilitating the energy flow.

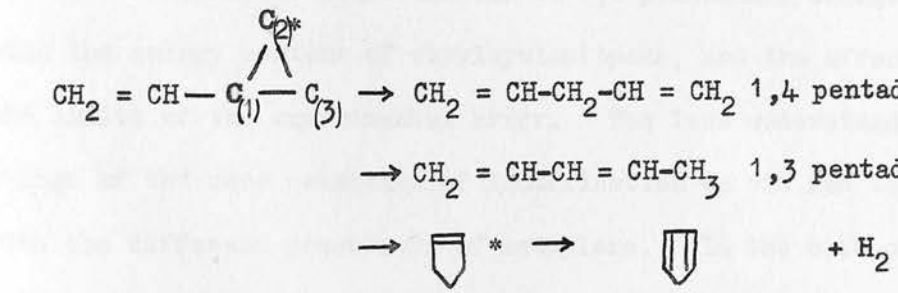
Additional support for energy flow comes from experiments in which the same molecule is formed in different states of vibrational excitation, like 1-methyl cyclopropane from addition of methylene to cyclopropane and propylene[41].

In the first case the whole vibrational energy is localised at the methylgroup - outside the cyclopropane ring; the same (within the limits of the experimental error) distribution of products as in the isomerization of CH_3-$\triangle$ formed from propylene and CH_2, where the excess energy is situated within the ring, confirms the conclusion that equilibration of vibrational energy is a fast process.

Another example of the energy flow is given in the decomposition of the activated secondary butylradicals formed by the addition of the H-atoms to butene-1 and butene-2[90]; again, although the radicals are formed in the different ways, they decompose at virtually the same rate describable by the same model, in which energy can migrate freely before the decomposition.

All this evidence implies that the Slater's model does not apply rigorously to molecules in the higher vibrational states, still it can be valid for molecules excited thermally in lower vibrational states, where this energy is distributed uniformly.

The variant of structural isomerization is the case reported in this work in which vinylcyclopropane formed from the addition of methylene to butadiene undergoes not only isomerization to 1,3- and 1,4-pendadienes but also re-arrangement to cyclopentene. This could be due to the opening of the cyclopropane ring forming the biradical $CH_2 = CH-\dot{C}H-CH_2-\dot{C}H_2$ in resonance with $\dot{C}H_2-CH_2-CH = CH-\dot{C}H_2$ which can cyclize to the more thermodynamically stable five membered ring of cyclopentene. The last compound is still excited and is able to lose a hydrogen molecule with the formation of cyclopentadiene. The energy of the cyclopentene must be greater than 58 kcals, i.e., the activation energy for the last process[91]. The isomerization of the excited vinylcyclopropane can thus be described as follows:



The activation energy for the isomerization to cyclopentene of 49.6 kcal/mole, much lower than the "normal" isomerization to the straight-chain pentadienes, is the reason why the thermal isomerization of vinylcyclopropane produces predominantly cyclopentene[84], with only 1% of the dienes. This is understandable as the heat of formation of cyclopentene (7.87 kcal/mole[94]) is much lower than those of pentadienes. ($\sim$ 30 kcal/mole).

In the present work this results in the higher rate of isomerization compared with the other C_5 cyclopropane derivatives, and also, due to the higher energy content than in the thermal work, these two modes of isomerization have comparable rate constants; the cyclopentene formation becomes less important in favour of pentadienes.

Thus in the case of the less energetic vinylcyclopropane from keten, the ratio of the cyclopentene-formation rate constant to the total rate constant of isomerization is equal 0.46, the more energetic diazomethane as the source of methylene brings down this value to 0.28 which is compensated by the increase in the rate constants of isomerization to the pentadienes.

The higher energy content of vinylcyclopropane derived from diazomethane is also reflected in the more energetic cyclopentene: the rate of its decomposition to cyclopentadiene and hydrogen is greater by a factor of 2 in this case than in the reaction of beten.

The rate constant of isomerization to 1,4-pentadiene changes very slightly with the energy content of vinylcyclopropane, and the effect may well be within the limits of the experimental error. The less understandable point is the change of the rate constants of isomerization to cis and trans 1,3-pentadienes with the different precursors of methylene. In the case of keten the rates for the cis and trans isomers are very similar with a slight tendency to favour the trans-isomer, and the total rate of isomerization to 1,3-pentadienes (^{k} cis + ^{k} trans) is equal to the rate of isomerization to 1,4 pentadiene. This tendency is enhanced in the case of diazomethane as the methylene source, and the sum ^{k} cis + ^{k} trans is larger than ^{k} 1,4 pentadiene. The last fact could suggest some steric hindrance for isomerization to 1,3 pentadienes being surmounted by the more energetic molecules.

The larger k_{trans} than k_{cis} could be attributed to the cis-trans isomerization, examples of which were found in other instances of cyclopropane derivatives[1] isomerization.

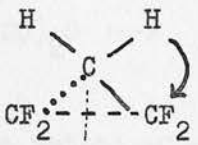
Both 1,3 and 1,4-pentadienes are formed by the rupture of the C_1-C_2 or C_1-C_3 bond, β to the double bond. The constancy of the isoprene yield throughout the investigated range of pressure suggests that the breaking of the C_2-C_3 bond does not occur. This is understandable if we assume formation of the biradical by a direct rupture as the first step of the isomerization, as the β cleavage forms a stable allylic radical. No such a radical can be produced by the breaking of the γ C_2-C_3 bond.

Two mechanisms of the cyclopropane isomerization are conceivable; Slater's calculations are based on the assumption that the hydrogen migration before the opening of the ring is the rate determining step. Rabinovitch, Schlag and Wiberg[95] interpreted their finding of the geometrical isomerization of trans 1,2 dideuterated cyclopropane being faster than structural isomerization as evidence against the hydrogen migration mechanism; and in favour of the formation of the open trimethylene biradical as the primary step.
The last assumption would imply the C-C bond as the critical co-ordinate (instead of Slater's distance between carbon atom and the hydrogen attached to the adjacent carbon) and would lead to n = 3 inconsistent with the experimental data.
The existence of the trimethylene radicals in the cyclopropane isomerization has not been confirmed in the experiments where these radicals were expected to react with some radical-scavengers[96,97]. However as it was pointed out the rates of recyclization or re-arrangement of the trimethylene radicals are much faster than the rates of the above reactions[98,99]; hence the non-existence, or rather non-detectability, of the radicals may be fortuituous.

Smith[100] indicated that the results of Rabinovitch could be interpreted in terms of the partial hydrogen migration; the transition state would involve the CH_2 group rotating unless it is coplanar with the ring. The hydrogen migration before the CH_2 group left the planar configuration could lead to ring opening. Frey[83] discussed the results of 1,2 dimethylcyclopropane isomerization assuming the modification of Rabinovitch's scheme - a ring enlargement with the accompanying hindered rotation. The problem remains still open; the conclusion reached so far is that the hydrogen transfer is not important to a great extent - the C-C bond is the factor responsible for the cyclopropane isomerization. Whether this bond is completely broken and the two end groups are free, or whether it is only expanded in the transition state has yet to be solved.

The fact that vinylcyclopropane does not undergo γ -rupture, consistent with the smaller amount of isobutene from the corresponding cleavage in 1-methycyclopropane, could be ascribed to the stronger C_2-C_3 bond (less substituted than C_1-C_2 or C_1-C_3). Similarly if we attempt to apply Smith's mechanism - the γ -rupture would involve the rotation of the heavy $C\begin{smallmatrix}-H\\ \diagdown CH = CH_2\end{smallmatrix}$ group with the large moment of inertia compared with the light CH_2 group. That could be responsible for the lower probability of the C_2-C_3 breaking. In the light of the fact that this probability is equal to zero the most probable process seems to be the formation of the stable biradical by the β -rupture which supports the Rabinovitch's mechanism. An example of the isomerization of a cyclopropane derivative containing hetero-atoms is the case reported in the present work of the isomerization

of 1,1 2,2 tetrafluorocyclopropane. The presence of the fluorine atoms in the molecule introduces new factors; the bond strengths are not the same as in the cyclopropane molecule and also there exist two possibilities of migration accompanying rupture; one involving the hydrogen atom and one involving the fluorine atom. The structure of the only product of isomerization found suggests that only the CF_2-CF_2 bond undergoes rupture and only the hydrogen atom is shifted, as is shown below:



···· - bond to be doubled
--- - bond to be broken

This is conceivable as the CF_2-CF_2 bond is weaker than the CH_2-CH_2 bond and also the migration of the lighter hydrogen atom is more feasible than movement of the heavier fluorine atom. The $\frac{k_{isom}}{k_{deact}}$ ratio equal to 3.6 atm. is $\sim$ 3 times larger than the corresponding ratio for the cyclopropane isomerization. As there are three times as many possibilities of the hydrogen migration in the cyclopropane molecule than in tetrafluorocyclopropane, the larger k_{isom} in the latter case could suggest that the hydrogen migration is not the rate determining step. In accordance with Rabinovitch's mechanism, or the ring-expansion mechanism, the strength of the C-C bond seems to be the more important factor in this isomerization.

CHAPTER II

GENERAL EXPERIMENTAL

2.1 MATERIALS

Keten: The thermal decomposition of acetic anhydride (M & B) at 500°C, proceeding according to the scheme:

$$(CH_3CO)_2O \longrightarrow CH_2 = CO + CH_3COOH$$

was employed as a method of preparing keten.

The apparatus used, similar to that used for the low pressure pyrdysis of propionaldehyde[105] is shown in Fig.1.

Acetic anhydride in tube A, boiling under reduced pressure was passed through the quartz reaction chamber Q placed in the furnace C, where decomposition took place. Acetic acid, together with unreacted acetic anhydride were condensed in the trap D, kept at dry ice-acetone mixture, keten was trapped in E, cooled in liquid nitrogen. Dimerization, which is the main source of impurities was prevented by the flow system and working under reduced pressure. Further purification was effected by the bulb-to-bulb distillation from dry ice-acetone to liquid nitrogen, rejecting the head and tail fractions. It was stored as a solid at liquid nitrogen temperature to prevent the dimerization and decomposition.

No impurities detectable by gas-chromatography were found.

Bp. = -56°C

Diazomethane was prepared by the action of N-methyl nitrosourethane (L.Light CO) on KOH in ethylene glycol;

$$CH_3N(NO)COOC_2H_5 + 2KOH \rightarrow CH_2N_2 + K_2CO_3 + C_2H_5OH + H_2O$$

N-methylnitrosourethane was introduced gradually through a dropping funnel into a flask containing KOH in ethylene glycol (12g KOH/45ml.ethylene glycol) kept at 40°C.

The diazomethane evolved was continuously swept by a stream of dry nitrogen through a coil cooled in an ince-salt mixture and condensed in atrap immersed in liquid nitrogen, where it was stored in small quantities.

Except for degassing it prior to each experiment no other purification was carried out. Gas chromatographic analysis showed it to be 99% pure.

Bp. = -23°C

1,3 butadiene: Butadiene sulphone (British Celanese Ltd.) served as a starting material for preparation of this reagent. It decomposes on heating to SO_2 and butadiene. On passing the decomposition products through a wash-bottle containing 20% aqueous KOH, and successively through dryers filled with KOH pellets, SO_2 was absorbed, butadiene condensed in the dry ice-acetone cooled trap. It was then degassed and purified by several bulb-to-bulb distillations over KOH pellets, and finally stored as a gas. No impurities were detected by gas chromatography.

Bp. = -4.5°C

Butene-1 was made from N-butyliodide (B.D.H.) by the reaction with 20% alcoholic KOH. Iodide from a dropping funnel was added to a flask, heated on a water bath and provided with a reflux condenser. The butene-1 evolved was collected at the top of the condenser in the trap kept in dry ice-acetone slurry.

It was degassed and distilled to the relevant bulb-rejecting the tail fraction.

Bp. = -6.26°C

Pentene-1 (L.Light Co.) was degassed and distilled under reduced pressure from ice-salt to dry ice-acetone temperature with rejection of the head and tail fractions. The purity was 99.5%.

Bp. = 29.9°C

Tetrafluoroethylene was a gift from I.C.I. Ltd. - Plastics Division. As it had to be transferred from the original container by replacing it with water, this last compound was the main impurity in addition to small amounts of perfluorocyclobutane. Before putting it into the storage bulb it was then dried with $CaCl_2$ and KOH pellets, degassed and distilled from the dry ice-acetone to liquid-nitrogen temperature. It was stored as a gas.

Bp. = -76°C

Neopentane was the commercially available (Matheson & Grade) sample, claimed to be 99.5% pure. It was used without purification, as the gas chromatography analysis confirmed its purity.

Bp. = 9.5°C

Cyclopentene was made by the reaction of cyclopentyl bromide with alcoholic KOH[107]. It was purified by distillation collecting the fraction boiling at 44°C.

Bp. = 44°C

Cyclopentadiene was prepared by thermal cracking of the cyclopentadiene dimer[106], purified by fractionating and redistilled.

Bp. = 40.6°C

Oxygen, nitrogen and argon were B.O.C. Ltd. products, dried and purified from all condensables by passing through a column of celite immersed in the liquid oxygen.

2.2 APPARATUS AND PROCEDURE

The kinetic apparatus employed in this investigation was a conventional vacuum system constructed of Pyrex glass and is shown in Fig. 5. The two stage mercury diffusion pump backed by the "Speedivac" rotary oil pump formed the pumping system. This set-up enabled us to reduce the pressure to 10^{-5} mm.Hg. as shown by the McLeod gauge, after about 30 minutes pumping. The storage vessels consisted of 21 bulbs with traps for condensation and "degassing" of the contents.

Several reaction vessels constructed of Pyrex glass or quartz were used throughout the experiments. The volumes varied between 10-2000cc, to supply a sufficient amount of products for analysis even in the low pressures experiments. They were kept at room temperature by means of a stream of water running smoothly over the surface.

The pressure in the system was measured with a mercury manometer, or in the experiments at low pressures where the limit of accuracy of the manometer was reached, by a dosing system. In the last method the pressure of the reactants was first measured in a volume ~ 5-100 times smaller than the volume of the actual reaction vessel, in which the reaction mixture was then expanded. The "sharing ratio" of these two volumes had been previously determined using relatively large amounts of pure reactants.

The volumes of the reaction vessels are given below with reference to the range of pressure in which they were used.

	Pressure /mm.Hg./	Volume of the RV /cc./	The sharing ratio
Pyrex RV[1]S	760-200	14.5, 10.2	-
	200-15	52.5, 63, 56.8, 49.0	-
	15-5	242	14.4
	5	1000, 2000	52.0 70
Quartz	760-200	10.8	-
	200-15	65.0	-
	15-5	576	23.5

Replacement of the reaction vessels of small volume was necessary after several experiments because the nonvolatile liquid was deposited on the walls.

Lamp. A medium pressure 125 Watt mercury arc (Osram) was used as the source of irradiation. It was shielded with an aluminium foil reflector. Polychromatic radiation was employed throughout the whole work.

Procedure. The apparatus was evacuated until a pressure of about 10^{-5} mm.Hg. was obtained in all parts of the system open to the main vacuum line; the reactants were condensed and degassed at the same time. Having obtained a satisfactory vacuum keten or diazomethane were allowed in to the reaction vessel from the trap k or D, and the pressure noted. (For the sake of safety, trap D containing diazomethane was detachable. It was stored in a shielded "safety cupboard" and transferred prior to the experiment to the apparatus.) The residual keten or diazomethane in the R line were then condensed back and the line evacuated again. The pressure of the second component of the reaction mixture was then allowed to develop in the line R until it slightly exceeded the pressure of keten in the reaction vessel.

Tap b was then opened until the total pressure reached the required value, the pressure of the second component being 2-5 times greater than that of keten. The back-diffusion of keten was minimized by employing an excess of the other component, and connecting the reaction vessel to the rest of the vacuum system with 20 cm. long fine capillary. The mercury lamp was switched on, left shielded for 15 minutes to allow it to warm up, and the reaction vessel was then exposed to the light for a subsequent 30 minutes. After that time the contents of the reaction vessel were condensed in trap I at liquid nitrogen temperature. All non-condensables were pumped off, and all condensables injected to the gas chromatography columns; taps i_1 and i_2 were open as in Fig. 5, to allow the stream of hydrogen to flow through I, and the mixture to be injected was warmed up with boiling water. The reaction products were then analyzed on the chromatographic column.

In the experiments with tetrafluoroethylene carried out at high pressures, a known amount of reaction mixture was condensed in a small ampoule of predetermined volume. A capillary tube connecting it with the rest of the apparatus was then sealed off under vacuum and the contents of the ampoule allowed to warm up before irradiation.

After the reaction took place, the reactants and products were again condensed at liquid nitrogen temperature, left at this temperature for 5 minutes to ensure complete condensation, then the seal was broken and the ampoule reconnected to the main apparatus. After degassing, the reaction mixture was transferred to I and analysed in the usual manner.

2.3 THE ANALYTICAL APPARATUS

Gas chromatography was employed for analysis throughout the present work.

Quantitative studies of more complex methylene reactions, whose products, being isomers, are difficult to separate, would not be possible without gas chromatography.

G.L.C.[≠] was used in all cases except for the analysis of the methylene-C_2F_4 reaction where G.S.C.[≠] was employed. A thermal-conductivity gauge - katharometer, served as a detector and hydrogen as a carrier gas. The details of column packings are given in the following section.

Products were identified by comparing the retention times of standard samples with those of the products supplemented where necessary by infra-red analysis. Peak areas on chromatograms were taken as a measure of the quantity of products. The ratio of these areas was equal to the relative amount of products, assuming that each product had the same thermal conductivity. As the products were always isomers, containing the same number of carbon atoms this assumption is probably correct within 1-2%.

The scheme of the gas chromatographic apparatus is given in Fig. 3. The stream of hydrogen from the commercial cylinder was split after passing the dryer of molecular sieve: one part of the stream passed through the mercury and water bubbler, the height of which controlled the pressure of the gas, i.e., the flow rate, the second part flowed through buffering vessels to the rest of the chromatographic set-up. The buffering vessels consisted of a series of small tubes joined by fine capillary tubing, by means of which all irregularities of flow were smoothed. After emerging from the buffering vessels hydrogen passed through the "balancing" arm of the detector to be split again

[≠] G.L.C. - gas liquid chromatography
G.S.C. - gas solid chromatography

at the injection system. This was formed by the U-shaped glass tube of 1cc. volume and served at the same time as a trap for condensing products from the reaction vessel (I on Fig. 5). The gas could flow through it, or alternatively, when it was evacuated, through the by-pass made of the fine capillary. After passing the injection system the hydrogen was fed into the analysing column, then passed through the "detecting" arm of the detector to be finally let into the atmosphere. The dibutylphthalate flow-meter situated at the end of the whole system measured the flow rate. It was calebrated with a "soap bubble" flow-meter to get the absolute value of the flow rate. When the products after having been separated in the columns were collected for the i.r. analysis, the flow-meter was replaced by a special trap. (The details of the collecting procedure and construction of the trap are given in J. H. Knox "Gas Chromatography"[108] and Anderson's paper on the applications of the i.r. analysis in connection with gas chromatography[109].)

The columns and conditions of their operation. The chromatographic columns were made of glass tubing 4mm. diameter in cases where analysis was carried out at room temperature, or had the form of a copper coil when the conditions required a reduced temperature. In the first case they were contained in a fibreglass jacket, in the second in a Dewar flask filled with an ice-water slurry.

The 80-100 mesh celite (Gas Chromatography Ltd.) was used as the solid support in cases where G.L.C. was applied, alumina poisoned with 1% dinonylphthalate was the packing in the G.S.C. case. The liquid phase was deposited on the solid support by the usual way of dissolving it in the low boiling solvent, mixing with celite and evaporating the solvent off under reduced pressure (water pump). The packing was then dried for 2-12 hours

(depending on the vapour pressure of the liquid phase). Table 2.1 gives the details of the columns used in the experiments, with the condition of their operation. The last column of this table enumerates the products separated on the given column with their retention times-R_t's in cm. (the chart speed of the recorder being 0.85cm. per minute).

The columns were working at a flow rate close to the optimum flow rate, the values of which were in some cases determined from the Van Deemter curve. Fig. 2 shows such a curve for column 1 (5% squalane on celite) operating at room temperature, obtained by measuring HETP* at various flow rates. (HETP = $\frac{l}{N}$, where l is length of the column and N is the number of theoretical plates, was calculated from the experimental data by applying the well known formula: $N = 5.54\frac{(Rt)^2}{(\Delta t)}$, where R_t represents retention time, Δt - the peak width at half-height of peak.) The optimum flow rate ~ 35ml/min. (Fig. 2) increased to ~ 50ml/min. where the temperature was altered from room temperature to 0°C.

*HETP - height equivalent to a theoretical plate

TABLE 2.1

No.	Column packing	Length /m/	Diam. /mm/	Flow rate /ml/min./	Compounds	R_t /cm/	Temp. °C
1	5% squalane on 80-100 celite	6.5	3	45	1,4 pentadiene	7.2	0°
					isoprene	10.5	
					vinylcyclopropane + trans 1,3 pentadiene + cyclopentadiene	13.2	
					cis 1,3 pentadiene	14.8	
					cyclopentene	18.2	
				35	4 methyl + 3 methyl pentenes-1	10	Room temp.
					2 methyl pentene-1	12.2	
					hexene-1	14.1	
					hexene-2 (trans)	17.8	
					propylcyclopropane + hexene-2 (cis)	19.0	
2	5% squalane on 80-100 celite + 20% squalane on 80-100 celite	6.5 + 1.5	3 + 3.5	30	3 methylbutene-1	8.7	Room temp.
					pentene-1	12.2	
					2 methylbutene-1	13.5	
					pentene-2 (cis & trans)	15.8	
					ethylcyclopropane	16.8	
					2 methylbutene-2	18.1	
3	15% acetonyl acetone on 80-100 celite	8.5	4	50	1,4 pentadiene	10.2	0°
					isoprene + cyclopentene	17.2	
					1,3 pentadiene	23.4	
					vinylcyclopropane	24.7	
					1,3 pentadiene	26.5	
					cyclopentadiene	32.5	
4	1% dinonyl-phthalde on alumina (60-90)	5.5	3	45	tetrafluoropropylene	6.4	0°
					tetrafluorocyclopropane	14.3	

Detector

The thermal conductivity cell (katharometer) was used as a detector. This was made of a brass block with two channels bored through it, which had two identical tungsten filaments of resistance approximately 10 ohms. each, stretched across them. The filaments formed two arms of the Wheatstone bridge, the other two arms consisted of standard 100 ohm resistances. The 10,000 ohm rheostat in parallel with one of these resistances was used to adjust the balance of the bridge. The off-balance potential, reflecting the change in thermal conductivity in the "detecting" side of the katharometer when a component of the analysed mixture was passing, was recorded on the 1 mV Honeywell-Brown recorder. The voltage for the bridge was supplied by two 2 volt batteries. The electrical circuit is shown in Fig. 4. The areas of the peaks, each of which represented a single component of the analysed mixture, were then planimetered.

CHAPTER III

REACTIONS OF METHYLENE WITH 1,3 BUTADIENE AND ISOMERIZATION OF EXCITED VINYLCYCLOPROPANE

Summary. The addition of methylene from keten and diazomethane to 1,3 butadiene, followed by isomerization of excited vinylcyclopropane has been studied.

A mechanism that accounts for the rates of formation of the principal products was postulated. The relative rate constants of the primary reaction were estimated. The rate constants of isomerization of vinylcyclopropane to various olefins and cyclopentene were obtained on the assumption that the rate of deactivation of the excited vinylcyclopropane is 10^{10} sec.$^{-1}$atm.$^{-1}$.

A summary of the data is given in table 3.1. The feature which differentiates the vinylcyclopropane isomerization from the analogous process of other cyclopropane derivatives is formation of cyclopentene, which is capable of decomposing to cyclopentadiene and a hydrogen molecule.

Results. The reaction mechanism postulated for this reaction by analogy with the reactions of methylene with olefins was:

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \quad (a)$$

or

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2 \quad (b)$$

$$CH_2 + CH_2 = CH-CH = CH_2 \xrightarrow{k_1} CH_2\!\!<\!\!\begin{matrix}CH_2\\ |\\ CH\end{matrix}\!\!-CH = CH_2^{*} \quad (1)$$

$$\xrightarrow{k_2} \text{cis } CH_2 = CH-CH = CH-CH_3 \quad (2)$$

$$\xrightarrow{k_3} \text{trans } CH_2 = CH-CH = CH-CH_3 \quad (3)$$

$$\xrightarrow{k_4} CH_2 = C(CH_3)CH = CH_2 \qquad (4)$$

$$\text{cyclopropyl-}CH_2^{*} + M \xrightarrow{k_6} \text{cyclopropyl-}CH_2 + M \qquad (5)$$

$$\text{cyclopropyl-}CH_2^{*} \xrightarrow{k_7} \text{cis } CH_2 = CH-CH = CH-CH_3 \qquad (6)$$

$$\xrightarrow{k_8} \text{trans } CH_2 = CH-CH = CH-CH_3 \qquad (7)$$

$$\xrightarrow{k_9} CH_2 = C(CH_3)CH = CH_2 \qquad (8)$$

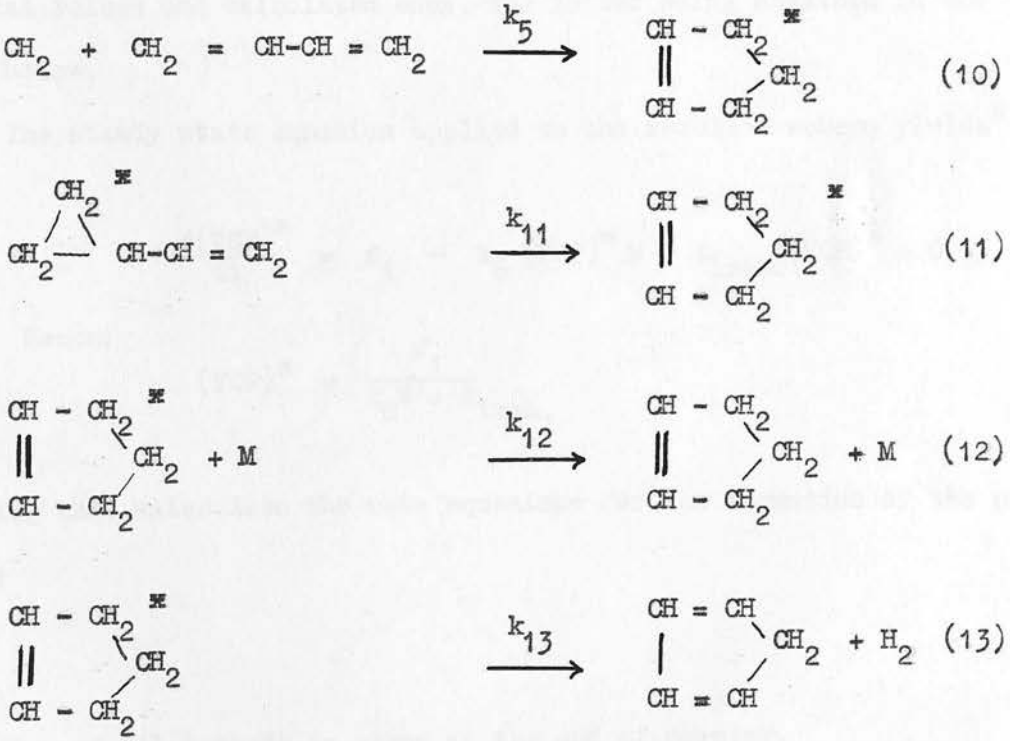
$$\xrightarrow{k_{10}} CH_2 = CH-CH_2-CH = CH_2 \qquad (9)$$

The possibility of adding methylene to two ends of the butadiene molecule to form cyclopentene was excluded in the early stages of the present work on the grounds that the R_t of the standard sample (L. Light Co.) did not correspond to the R_t of any of the products.

After a good deal of work had been done on variation of the yields of products with pressure it was reported by Frey[96] that the thermal decomposition of vinylcyclopropane yielded cyclopentene as a main product, and Franzen[107] obtained some cyclopentene from the reaction of butadiene with diazomethane in solution. We therefore re-investigated the reaction and found that due to impurities in the standard samples we incorrectly identified cyclopentene as cis 1,3 pentadiene, whereas in fact this last compound was contained in the "vinylcyclopropane" peak. The cyclopentene made from cyclopropyl bromide gave a R_t corresponding exactly to the R_t of the product in question, and the i.r. analysis confirmed the presence of cyclopentene in the reaction.

In addition, a column packed with acetonyl acetone resolved the "vinylcyclopropane" peak in experiments at low pressures, giving an extra product identified later as cyclopentadiene.

The decrease in the cyclopentene yield with the accompanying increase in the yield of the former product suggested that the latter was derived from the former. This was confirmed by a check-experiment of the pyrolysis of cyclopentene at 500°C, which yielded mainly this product - in addition to a small amount of low-boiling hydrocarbons. As it was shown by Vanas and Walters[91] that the main product of the cyclopentene decomposition is cyclopentadiene, and as gas chromatography showed that the R_t's of the pure cyclopentadiene and of the product investigated were identical it was concluded that the product in question was cyclopentadiene. It was corroborated by i.r. analysis. In light of the above findings the following reactions were added to the scheme:



$$CH_2 + CH_2 = CH\text{-}CH = CH_2 \xrightarrow{k_5} \text{(cyclohexene-3 diradical)}^{*} \qquad (10)$$

$$\text{(bicyclo[3.1.0]hexane diradical)}^{*} - CH\text{-}CH = CH_2 \xrightarrow{k_{11}} \text{(cyclohexene-3 diradical)}^{*} \qquad (11)$$

$$\text{(cyclohexene-3 diradical)}^{*} + M \xrightarrow{k_{12}} \text{cyclohexene-3} + M \qquad (12)$$

$$\text{(cyclohexene-3 diradical)}^{*} \xrightarrow{k_{13}} \text{1,3-cyclohexadiene} + H_2 \qquad (13)$$

Tables 3.2 and 3.3 give the data on the yields of all products at various pressures ranging from atmospheric pressure down to ~ 1mm.Hg. for two series of experiments with diazomethane and keten , obtained using the acetonylacetone column. This is supplemented by table 3.2[1] summarising the data of early experiments with the squalane column, on which cis 1,3 pentadiene and cyclopentadiene were not separated. Cyclopentene and isoprene were not resolved on the former column, however, as the early experiments showed that the isoprene yield is not affected by pressure, the change in the amount of cyclopentene + isoprene could be ascribed to a variation in the cyclopentene yield. The last value was then obtained by subtracting the fraction of isoprene from the total value of cyclopentene + isoprene. The early experiments also supply data on the cyclopentene yield so that this value can be doubly checked. Two series of values of the yields of products are given in table 3.2; 3.3 experimental values and calculated ones, the latter being obtained in the way described below.

The steady state equation applied to the reaction scheme yields*:

$$\frac{d(VCP)^*}{dt} = f_1 - k_6 (VCP)^* M - k_{isom.} (VCP)^* = 0$$

Hence:

$$(VCP)^* = \frac{f_1}{k_6 M + k_{isom.}}$$

Substituting this value into the rate equations for the formation of the products we obtain:

*Meaning of all symbols is given at the end of chapter.

$$R_{VCP} = f_1 \frac{k_6 M}{k_6 M + k_{isom.}} \qquad (a)$$

$$R_{cis.1,3PD} = f_2 + f_1 \frac{k_7}{k_{isom.} + k_6 M} \qquad (b)$$

$$R_{trans.1,3PD} = f_3 + f_1 \frac{k_8}{k_{isom.} + k_6 M} \qquad (c)$$

$$R_{IS} = f_4 + f_1 \frac{k_9}{k_{isom.} + k_6 M} \qquad (d)$$

$$R_{1,4PD} = f_1 \frac{k_{10}}{k_{isom.} + k_6 M} \qquad (e)$$

Generally, the yield of product x of the reaction investigated is equal:

$$R_x = f_x + \frac{k_x}{k_6 M} \times \frac{f_1}{1 + \frac{k_{isom.}}{k_6 M}} = f_x + \frac{k_x}{k_6} \times \frac{R_{VCP}}{M} \qquad (g)$$

A plot of $\frac{1}{R_{VCP}}$ versus $\frac{1}{M}$ should be a straight line according to the above equations, with $\frac{1}{f_1}$ as the intercept and $\frac{k_{isom.}}{f_1 k_6}$ as the gradient. Plots of yields of products vs. $\frac{R_{VCP}}{M}$ should also produce a straight line with intercept equal to f_x and gradient to $\frac{k_x}{k_6}$.

By means of equation (g) we can calculate then the value of the yield of products at any pressure, preferably using the calculated (eqn.a) yield of vinylcyclopropane-R_{VCP}. Any systematic difference between experimental and calculated values would be reflected as a curvature in the plots. The plots obtained for

the diazomethane series of experiments were linear within the limits of experimental error, the ones for the keten series were slightly curved at low pressures. The curvature was in the sense that k_7, k_8 and k_{10} decreased slightly with increase of pressure, while k_{11} increased. Only the last of these trends is in a direction which could be predicted by an energy spread of the activated molecules. The curvature is however only just within reasonable estimates of the experimental error and may not be real. In figures 6-9 the experimental results are plotted. The lines represent the values calculated in the above manner, the points are the actual experimental values. Except at very low pressure the agreement is good.

Values of $f_1 - f_5$ and $k'_x s^{\neq}$ calculated are given in table 3.1.

Mechanism of the vinylcyclopropane isomerization. As the plots and table 3.2 suggest, vinylcyclopropane isomerizes to cyclopentene, 1,3 and 1,4 pentadienes. No change in the isoprene yield was observed throughout the whole range of pressure, which implies that this compound is derived only from the primary attack of methylene on the $=\overset{1}{\underset{H}{C}}-$ bond in butadiene.

The rates of isomerization to pentadienes and cyclopentene are different for the two series of experiments with ketene and diazomethane. The overall rate of isomerization is 4.7 times larger in the diazomethane series than in the ketene one. The fraction of vinylcyclopropane isomerizing to cyclopentene $\frac{k_{11}}{k_{isom.}}$ is larger in the second case. There is also a difference in the fraction of vinylcyclopropane rearranging to the 1,3 pentadienes for the two series, the trans compound being favoured to the cis in the diazomethane experiments.

That could be due to the reaction:

cis 1,3 pentadiene $\longrightarrow$ trans 1,3 pentadiene

which is more likely to occur with the more energetic molecules derived from diazomethane.

The total fraction of vinylcyclopropane, which isomerises to the 1,3 pentadienes - $\frac{k_7 + k_8}{k_{isom.}}$ is however different in the two series in contrast to 1,4 pentadiene for which the ratio $\frac{k_{10}}{k_{isom.}}$ is almost the same in both cases.

Decomposition of excited cyclopentene. The steady state equation applied to this reaction in accordance with the general reaction schemes gives the following expression for the yield of cyclopentadiene:

$$R_{CPD} = \frac{f_1 k_{11}}{k_{isom} + k_6 M} \times \frac{1}{\frac{k_{12}}{k_{13}} M + 1}$$

As $\frac{R_{CP}}{R_{CPD}} = \frac{k_{12} M}{k_{13}}$, values of $\frac{k_{12}}{k_{13}}$ can be obtained from the appropriate plot. Values of k_{13} shown in table 3.1 are taken from this ratio assuming again the rate of the cyclopentene deactivation to be 10^{10} sec.$^{-1}$atm.$^{-1}$.

As table 3.1 shows, the cyclopentene decomposition being a unimolecular process, is also affected by the energy content of the reacting molecules: k_{13} is larger in the case of the diazomethane experiments than in the keten ones.

The primary attack of methylene on the double bond and the two types of vinyl C-H bond in butadiene is described by the values of f's in table 3.1, which represent a fraction of methylene reacting with a given bond to yield product "x". From the equation (g), $R_x = f_x$, when M approaches infinity. Values of f_x are hence equal to the values of fractional yields of products at infinite pressure and are obtained by extrapolation of the R_x VS $\frac{1}{M}$ curves to zero.

The ratio of the yields of products is then equal at this pressure to the ratio of rate constants:

$$f_1 : f_2 : f_3 = R_{VCP} : R_{1,3PD} : R_{IS} = k_1 : k_2 + k_3 : k_4$$

More relevant than the rate constants are values of rate constants per bond, obtained simply by dividing the first value by the number of bonds of the type under consideration in the parent butadiene, which are exposed with equal probability to methylene attack. (The differentiation between the rate of formation of product x - k_x, and the value of the rate constant per bond sometimes called the reactivity of the bond, might be a source of confusion. In the present work, the rate of attack of methylene on a given bond means the rate constant per bond.)

Reactivities of the bonds in butadiene estimated in the manner indicated above are as follows:

	C = C	$=CH_2$	=CH-C
keten	1	0.06	0.04
diazomethane	1	0.085	0.077

The difference between the values for the two sources of methylene is in the direction expected from the higher energy content of the methylene derived from diazomethane.

The values of the cyclopentene yield at high pressures suggest that some cyclopentene is formed by a direct addition of methylene to two ends of the butadiene molecule. Even if we assume that the value of $f_{cyclopentene}$ is (within the limits of experimental error) equal to zero, in the keten series, the higher value in the diazomethane experiments (3%) suggests that cyclopentene is also formed in the primary attack.

The values of the cis and trans 1,3 pentadiene yields at high pressures in the ketene experiments imply equal rates of formation of both isomers. In the diazomethane series the $\frac{cis}{trans}$ ratio is different, the cis-compound being favoured over the trans.

Note:

Abbreviations and symbols used in the preceding chapter have the following meaning:

VCP - vinylcyclopropane

CP - cyclopentene

CPD - cyclopentadiene

PD - pentadiene

IS - isoprene

R_x - yield of product x

k_i - rate constant of reaction (i) (i - 1 - 13)

f_x - fraction of methylene reacting to produce product x

k_{isom} - total rate constant of isomerization equal to $\sum_{i=7}^{11} k_i$

Table 3.1
Rate constants for the methylene addition to butadiene

Rate constant	Product	source of methylene: keten	source of methylene: diazomethane
f_1	VCP	0.87	0.78
f_2	cis 1,3 PD	0.048	0.084
f_3	trans 1,3 PD	0.045	0.048
f_4	IS	0.040	0.060
f_5	CP	0.010	0.030
k_6	VCP: assumed value 10^{10} sec^{-1} atm^{-1}		
k_r	all products[/]	2.6×10^8	12.3×10^8
k_7	cis 1,3 PD	0.35	1.7
k_8	trans 1,3 PD	0.42	3.3
k_9	IS	0.00	0.00
k_{10}	1,4 PD	0.75	4.1
k_{11}	CP*	1.20	3.5
k_{12}	assumed value: 10^{10} sec^{-1} atm^{-1}		
k_{13}	CPD + H_2	0.66	1.0
k_7/k_r	cis 1,3 PD	0.13	0.14
k_8/k_r	trans 1,3 PD	0.14	0.27

Table 3.1 (Contd.)

Rate constant	Product	source of methylene: keten	source of methylene: diazomethane
k_{10}/k_r	1,4 PD	0.28	0.33
k_{11}/k_r	CP	0.44	0.28

/All unimolecular rate constants are in sec^{-1} and are of the order of 10^8 sec^{-1}.

Table 3.2

Reaction of methylene with 1,3 butadiene

Keten as methylene source

Pressure (mm.Hg.)	% Yields of VCP exp.	VCP calc.	1,4 PD exp.	1,4 PD calc.	cis 1,3 PD exp.	cis 1,3 PD calc.	trans 1,3 PD exp.	trans 1,3 PD calc.	CP exp.	CP calc.	CPD exp.	CPD calc.
619	81.2	82.0	0.9	0.7	6.3	5.5	5.3	5.2	2.3	1.4		
545	82.0	81.3	1.2	0.84	5.7	5.6	4.8	5.3	2.3	1.6		
229	80.0	78.3	2.0	1.9	5.6	6.1	5.2	5.8	4.2	3.6		
132	76.5	73.6	2.5	3.1	5.7	6.7	5.3	6.6	6.0	5.9		
114	73.3	72.2	3.5	3.5	5.2	6.9	6.2	6.8	7.8	6.7		
82	66.6	68.2	6.4	4.7	7.0	7.3	6.9	7.3	10.1	8.3		
80	67.0	67.8	11.4	4.8	6.9	7.5	7.4	7.5	10.3	8.5		0.5
49	64.0	60.2	6.1	7.1	5.8	8.2	8.4	8.8	11.7	11.8	0.2	1.1
40	54.5	56.7	7.5	7.9	7.7	8.7	9.2	9.3	16.6	13.5	0.5	1.5
34	53.0	53.5	8.5	8.8	8.6	9.1	9.6	9.8	13.8	14.5	2.5	2.0
22	49.0	44.5	9.1	11.3	8.4	10.2	9.8	11.3	16.6	17.3	3.1	3.7
13	32.4	33.4	14.3	14.3	10.6	11.5	14.2	13.1	17.7	19.6	6.8	6.7
8.4	26.0	25.1	15.8	16.7	13.2	12.6	15.1	14.4	16.6	19.5	9.3	9.8
7.0	19.2	22.0	17.8	17.6	14.8	13.0	16.0	15.0	16.5	19.4	11.8	12.3
5.3	16.8	17.8	19.3	18.8	14.3	13.4	18.9	15.5	14.0	18.0	12.7	14.3
4.1	13.7	14.4	19.0	19.6	16.7	13.8	19.2	16.0	16.7	17.0	13.4	17.8
2.6	5.8	9.8	24.0	21.5	18.0	14.4	21.7	16.8	8.2	14.9	19.6	22.6
1.7	2.6	6.7	23.8	22.0	16.9	14.9	23.4	17.4	4.2	10.6	-	27.4
1.6	2.8	6.3	23.6	22.0	17.0	14.9	26.4	17.0	4.5	10.4	21.8	27.5

Table 3.3

Diazomethane as methylene source

341	61.0	61.0	4.9	5.5	11.6	9.7	9.1	8.9	7.3	7.8		
268	58.5	57.7	6.7	6.6	9.2	10.2	9.6	9.9	10.0	8.8		
210	54.5	58.9	8.8	8.0	9.5	10.8	10.8	11.0	10.4	9.9		
169	49.0	50.0	7.2	9.2	14.0	11.4	13.4	12.2	10.4	11.0		0.5
136	46.1	45.2	11.2	10.6	12.5	12.0	12.7	13.1	11.5	11.3		0.72
98	40.0	39.8	13.5	12.9	11.8	13.2	14.4	15.4	13.3	13.2		1.04
84	35.6	36.8	13.2	13.6	15.2	13.6	16.9	16.0	13.1	13.5		1.3
69	29.4	32.6	17.0	14.6	14.9	14.1	16.3	17.0	14.6	13.9	1.8	1.8
58	31.0	29.7	15.4	15.8	14.7	14.6	15.8	18.0	14.3	14.9	3.8	1.85
42	20.6	24.1	20.6	17.6	16.4	15.5	20.6	19.7	15.8	15.5	-	2.85
18.5	18.4	12.8	21.8	21.4	14.5	17.3	20.0	23.0	13.4	15.5	5.9	6.05
17.3	12.7	12.1	21.4	21.6	18.5	17.5	21.2	23.2	13.5	15.5	6.7	6.4
13.4	7.5	9.7	21.6	22.3	17.4	17.8	24.7	23.8	16.1	14.8	7.7	7.6
11.0	8.6	8.2	23.2	23.2	19.2	18.2	23.2	24.6	16.6	13.9	8.2	9.3
10.6	7.3	7.9	23.6	23.2	16.8	18.2	23.6	24.6	16.1	13.9	7.3	9.3
10.3	7.3	7.8	24.5	23.6	18.5	18.4	24.4	24.9	12.0	13.6	7.3	9.9
7.6	8.0	5.7	22.6	23.8	18.7	18.4	25.4	24.9	7.6	12.2	11.7	11.3
6.3	6.5	4.9	23.8	24.2	18.9	18.6	25.2	25.2	7.1	12.0	12.5	11.9
5.7	1.3	4.4	24.8	24.3	19.7	18.8	27.0	25.2	8.2	10.8	13.0	13.2
1.5	1	1.2	22.5	25.1	18.0	19.1	25.8	26.2	6.2	4.6	21.5	20.2
1.4	1	1.1	23.0	25.4	19.7	19.6	28.0	26.6	4.3	4.4	20.0	21.4

Table 3.2

pressure (mm. Hg)	% yields of VCP + trans 1,3 PD + CPD	1,4 PD	cis 1,3 PD	IS	CP
keten experiments - Pyrex R.V.					
760	90.1	1.6	3.6	2.5	2.2
501	89.5	1.6	3.5	3.6	2.8
258	87.0	2.8	4.5	3.0	2.8
202	82.0	4.6	4.2	4.1	5.1
178	84.0	3.2	5.1	2.0	5.1
145	79.4	4.0	5.4	4.7	6.5
123	78.0	3.8	7.1	3.5	7.6
83	76.7	3.2	7.9	2.6	9.6
75	71.0	6.8	7.0	3.1	12.1
31	67.6	7.8	8.9	2.6	13.1
14.6	58.3	11.9	11.5	2.4	15.9
10.2	55.0	15.6	9.2	3.9	16.3
9.8	54.0	15.4	10.8	3.6	16.2
6.2	47.5	18.7	15.1	2.6	16.1
4.8	49.6	19.3	15.5	4.0	11.6
3.8	45.8	21.6	16.7	3.3	12.5
1.7	46.5	25.8	20.8	2.1	4.7
1.0	48.0	26.0	19.0	2.5	4.6
0.6	48.5	25.0	18.4	4.0	4.1
0.6	48.2	25.1	20.0	3.8	2.9
0.3	49.0	22.0	21.0	2.9	unm
keten experiments - quartz R.V.					
650	88.5	2.9	3.3	2.9	2.4
455	88.0	2.8	2.8	3.6	2.8
315	85.0	3.8	3.8	3.6	3.8
210	81.0	6.0	4.2	3.0	5.8
145	77.2	6.9	5.4	2.7	7.7
128	77.5	8.6	3.8	3.2	7.5
104	76.0	9.2	4.6	2.5	7.6
81	74.5	11.1	3.8	2.5	8.1
55	74.0	10.1	4.1	3.7	8.1
30	57.6	17.7	5.2	2.1	17.4
22	49.6	26.6	4.0	3.2	16.6
18	48.0	26.6	8.0	2.7	14.7
6.4	48.6	26.7	10.2	3.6	10.9
3.7	45.5	29.0	11.4	3.2	10.8

Table 3.2 (Contd.)

pressure (mm. Hg)	% yields of VCP + trans 1,3 PD + CPD	1,4 PD	cis 1,3 PD	IS	CP
Diazomethane experiments - Pyrex R.V.					
733	81.0	3.1	4.6	7.5	3.8
448	75.5	5.2	6.6	6.1	6.6
257	67.0	8.3	8.3	8.1	8.3
184	65.5	9.9	8.3	6.4	9.9
122	60.5	10.6	12.9	6.2	9.8
71	54.5	14.6	15.0	5.8	10.1
47	52.5	17.3	15.7	5.5	10.0
17	46.3	20.4	18.5	5.4	9.4
9.8	40.0	26.0	21.0	8.0	5.0
5.7	42.5	27.0	21.0	5.4	4.1
5.7	41.5	25.0	23.3	8.2	2.0
Diazomethane experiments - quartz R.V.					
594	76.5	4.5	8.1	5.8	4.5
360	73.2	8.3	8.3	5.8	4.4
231	62.0	11.6	9.7	10.5	6.2
215	67.0	13.2	8.0	5.3	6.5
127	59.5	15.9	11.7	5.5	7.4
92	56.0	15.7	13.0	7.0	8.2
74	50.0	19.0	12.0	6.3	12.7
57	48.6	21.0	9.7	6.1	14.6
22	44.5	23.2	14.8	7.2	10.3
5.8	43.0	28.0	15.7	6.0	7.3
3.5	42.0	28.0	17.5	7.2	5.3

CHAPTER IV

REACTION OF METHYLENE WITH BUTENE-1

Summary. The reaction of methylene with butene-1 has been studied. The relative rates of attack of methylene on various bonds in butene-1 were determined using keten as a methylene source. The effect of inert gases on the rate of the primary attack has been investigated. The isomerization of the excited ethylcyclopropane was found to proceed with the rate $-0,04 \pm 0.01 \times 10^{-8}$ sec.$^{-1}$ for the diazomethane experiments, much lower than that of other C_5 cyclopropane derivatives.

4.1 EXPERIMENTAL

The kinetic apparatus was the same as described in Chapter II. The analysis was carried out using a 5% squalane on celite column (6m) in series with the 20% squalane on celite (1.5m). As ethylcyclopropane was not completely separated on this column, which could have obscured the expected change in its yield, the olefin absorbent column (0.6m) was incorporated in the system, prior to the ordinary column, so that the only saturated product ethylcyclopropane emerged from the system, all olefins being absorbed. The absorbent contained mercuric nitrate and mercuric acetate deposited on firebrick in the proportion recommended by Kerr and Trotman-Dickenson[111]. As the yields of products were measured relatively, neopentane was used as a marker. The mixture allowed to react with a methylene precursor, consisted of 17.5% of neopentane and 82.5% of butene-1.

Neopentane was chosen as a marker because of its clean reaction with methylene producing only neohexane. The last compound boils conveniently 12°C

higher than ethylcyclopropane so these two compounds could easily be separated.

With such an arrangement we could measure the ethylcyclopropane isomerization by following the change in the (ethyl cyclopropane)/(neohexane) ratio with pressure, provided that the neohexane yield is constant throughout the range of pressure, which is shown to be true by the results on the methylene insertion reaction.

4.2 RESULTS

The scheme postulated for the reaction in accordance with the experimental results can be pictured as follows:

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO \qquad (a)$$

$$CH_2 + CH_2 = CH\text{-}CH_2\text{-}CH_3 \xrightarrow{k_1} CH_3\text{-}CH_2\text{-}\overset{\ddagger}{\Delta} \qquad (1)$$

$$\xrightarrow{k_2} CH_2 = CH\text{-}CH_2\text{-}CH_2\text{-}CH_3 \qquad (2)$$

$$\xrightarrow{k_3} CH_2 = \underset{\underset{CH_3}{|}}{CH\text{-}CH}\text{-}CH_3 \qquad (3)$$

$$\xrightarrow{k_4} CH_2 = \underset{\underset{CH_3}{|}}{C\text{-}CH_2}\text{-}CH_3 \qquad (4)$$

$$\xrightarrow{k_5} CH_3\text{-}CH = CH\text{-}CH_2\text{-}CH_3 \qquad (5)$$

$$CH_3\text{-}CH_2\text{-}\overset{\ddagger}{\Delta} + M \xrightarrow{k_{deact.}} CH_3\text{-}CH_2\text{-}\Delta + M \qquad (6)$$

$$CH_3\text{-}CH_2\text{-}\overset{\ddagger}{\Delta} \xrightarrow{k_{isom.}} \text{pentenes}$$

Isomerization of ethylcyclopropane. Table 4.1 gives the values of the fraction of ethylcyclopropane at pressures ranging from 117-0.5mm. for two series of experiments with keten and diazomethane.

Table 4.1 Change of ethylcyclopropane yield with pressure*

KETEN EXP.		DIAZOMETHANE EXP.	
Pressure (mm.Hg.)	% yield of Et	Pressure (mm.Hg.)	% yield of Et
117	71.5	144	60
62	73.5	58	58.5
62	73.0	56	60.0
28	70.0	30	59.5
20	70.5	24	55.2
2.1	65.0	20	53.1
1.6	68.0	11	47.3
1.2	67.0	5	47.0
0.8	67.0	1.2	39.0
0.7	61.0	1.1	37.5
0.7	58.2	1.0	30.0
0.6	50.3		
0.5	50.1		
0.4	50.0		

*The results of experiments with neopentane as a marker (see 4.1)

As can be seen from this table, there is a decrease in the yield of ethylcyclopropane beginning from ~7mm. pressure in the keten reaction, and observable at higher pressures of ~20mm. in the diazomethane series.

The data on the keten experiments do not allow us to estimate the $k_{isom.}$ value, rough estimation of the $\frac{k_{isom.}}{k_{deact.}}$ ratio from the plot of $\frac{R_{ECP\infty} - R_{ECPp}}{R_{ECPp}}$ vs $\frac{1}{P}$ yields a value of 0.004 $\pm$ 1 atm. for the diazomethane series.

We conclude then that the isomerization of ethylcyclopropane does take place, although its rate is much lower than for the other C_5 cyclopropane derivatives. The structure of the compound in question is probably responsible for this.

The primary attack. Table 4.2 gives the results of experiments carried out with butene-1 and keten, estimating the relative yields of all products.

Table 4.2 % yields of products of reaction: butene-1 + keten

Pressure (mm.Hg.)	% Yield 3 Me-Bu-1	Pentene-1	2 Me-Bu-1	Pentene-2 *	Et-Δ
162	11.8	13.8	3.9	5.5	65
76	12.7	13.1	2.7	5.1	66.4
71	11.5	14.8	3.8	6.8	63.1
46	12.9	14.9	3.2	4.2	64.8
28	11.9	13.2	3.9	7.8	63.2
3.8	7.6	15.3	4.5	10.0	62.6
1.6	12.6	15.8	4.5	an.failure	61.5
Mean**	12.1	13.8	3.7	5.8	65

*Values represent cis + trans yield

**Mean of first five values at high pressures

As no change in their values occurs in the range of pressure 162-10mm., the mean of these values was taken as a measure of the yields at infinite pressure,

the ratio of which is equal to the ratio of the rate constants $k_1 : k_2 : k_3 : k_4$. From the reaction scheme we then get:

$$R_{\text{pentene-1}} : R_{3\ \text{MeBu-1}} : R_{2\ \text{MeBu-2}} : R_{\text{pentene-2}} : R_{\text{ethyl-}\Delta}$$

resulting from an attack on:

primary C-H	second. C-H	$\overset{H}{\underset{1}{}}C = C$	$\overset{H}{\underset{H}{}}\overset{1}{}C = C$	C = C bonds

is equal to:

$$k_2 : k_3 : k_4 : k_5 : k_1$$

which on substituting the numerical values of R's gives the ratio of reactivities:

$$\frac{13.8}{3} : \frac{12.1}{2} : \frac{3.1}{1} : \frac{58}{2} : \frac{65}{1}$$

The actual values of the relative reactivities are given in table 1.1.

Experiments with inert gases. Table 4.3 shows the data of the relative yields of products of the butene-1-methylene (from ketene) reaction carried out in the presence of a large excess of nitrogen, argon and oxygen.

Table 4.3

Gas	Reactant / Inert gas	% Yield Ethyl-Δ	3 MeBu-1	Pentene-1	2 MeBu-1	Pentene-2
-		65	12.1	13.8	3.7	5.8
Nitrogen	1:5	72.5	10.6	10.7	3.4	2.8
	1:9	71.4	9.6	12.1	3.1	3.8
Argon	1:4	68.5	9.4	15.7	3.4	3.0
	1:5	70.5	10.4	11.8	3.4	3.9
Oxygen	1:5	59.0	13.6	18.1	unmeas.	unmeas.
	1:5	62.0	14.4	16.6	unmeas.	unmeas.
	1:2.5	59.6	12.8	20.2	3.9	3.5

The incomplete separation of products prohibits us from making a definite conclusion about the effect of inert gases on the relative amounts of pentene-2 and 2 MeBu-1. However, one can see that the yield of ethylcyclopropane slightly increases in the presence of inert gas such as nitrogen or argon. This fact argues for some excitation of methylene from ketene. Oxygen present in the reaction mixture produces the opposite effect to that of argon or nitrogen; the yield of ethylcyclopropane decreases with the increase in the yield of olefins, particularly that of pentene-1. Besides this effect, the presence of oxygen brings about the decrease in the total yield of products: the amount of products under the same conditions of the reactant pressure and time of irradiation is approximately 5 times smaller in the presence of oxygen. Explanation of these facts is attempted in Chapter 1.3.

Additional products. At the experiments at low pressures two new products appeared in the amount ~ 2% of the total yields of products. Their R_t's on the analysing column corresponded to the R_t's of 2 methylbutene-2 and isopentane. The presence of the former could be due to the isomerization of 2-methylbutene-1. The possibility of its formation from the ethylcyclopropane isomerization seems to be very small, as such a process would involve highly improbable migration of two hydrogens, one of which would have to be transformed from the ethyl group - outside the cyclopropane ring. No reaction which could account for the isopentane formation at low pressures is feasible.

Note:

List of abbreviations and symbols in Chapter IV:

Et Δ	-	ethylcyclopropane
2 Me-Bu-2	-	2 methylbutene-2
3 Me-Bu-1	-	3 methylbutene-1
R_x	-	yield of product x
$R_{x\infty}$	-	yield of product x at infinite pressure.

CHAPTER V

REACTION OF METHYLENE WITH PENTENE-1

Summary. The reactions of methylene with pentene-1 are described. The values of the rate of attack of methylene on various bonds in pentene-1 are estimated to be very close to those of butene-1. No isomerization of propylcyclopropane was found.

5.1 EXPERIMENTAL

The kinetic apparatus was identical to that described in Chapter 2.2. The products were analysed on a 5% squalane column (column No.1 in table 2.3). As this column does not separate cis hexene-2 from propylcyclopropane, the amount of the former was taken as equal to the yield of the trans compound. 3 methyl- and 4 methyl-pentenes-1 also formed one peak on this column. As both these products are derived from the attack on the C-H bonds of the same type, the calculations of the rates of primary attack were not affected by their non-separation.

5.2 RESULTS

The experimental results can be explained in terms of the following scheme, analogous to the general scheme of the methylene-olefin reaction:

$$CH_2CO + h\nu \longrightarrow CH_2 + CO$$

or

$$CH_2N_2 + h\nu \longrightarrow CH_2 + N_2$$

$$CH_2 + CH_2 = CH-CH_2-CH_2-CH_3 \xrightarrow{k_1} CH_3-CH_2-CH_2-CH\begin{array}{l}/\,CH\\ \backslash\!-\!-\,CH_2\end{array} \qquad (1)$$

$$\xrightarrow{k_2} CH_2 = CH-CH_2-CH_2-CH_2-CH_3 \qquad (2)$$

$$\xrightarrow{k_3} CH_2 = CH-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \qquad (3)$$

$$\xrightarrow{k_4} CH_2 = \underset{\underset{CH_3}{|}}{CH}-CH-CH_2-CH_3 \qquad (4)$$

$$\xrightarrow{k_5} CH_2 = \underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3 \qquad (5)$$

$$\xrightarrow{k_6} CH_3-CH = CH-CH_2-CH_2-CH_3 \qquad (6)$$

Table 5.1 summarises data on the relative yields of products in the pressure range 728 to 5mm.Hg. for experiments with keten and diazomethane. No difference in the yields of products is observed in this range. It is therefore concluded that propylcyclopropane does not undergo isomerization. Evidently the pressure used is still sufficient to deactivate the excited propylcyclopropane and its excess energy is lost in collisions not by isomerization.
In the light of the results on the ethylcyclopropane isomerization (previous chapter) this finding is not unexpected.

The change of the reaction vessel from Pyrex to quartz does not bring about any change in the yields of products. This provides one more proof that the rate of methylene attack does not depend on the vibrational energy it possesses. The yield of products however changes with the source of methylene; diazomethane as the methylene source lowers the amount of propylcyclopropane in favour of olefins.

The rates of attack on the bonds in pentene-1 obtained in the usual way have the ratio:

C = C	primary C-H	secondary C-H	C = C(H)–	–C(H)=
53.2 :	5.1 :	5.9 :	2.4 :	2.4

in the keten experiments.

The corresponding ratio in the diazomethane experiments is:

43 :	6.2 :	6.2 :	4.0 :	4.0

Table 5.1 % Yields of products of reaction pentene-1 + CH_2

Pressure (mm.Hg.)	4Me-+3Me-Pentene-1	Hexene-1	% Yield cis He-2 + Pr-Δ	2 Me-Pentene-1	trans Hexene-2
Keten-Pyrex R.V.					
728	25.0	15.0	56.0	2.0	2.0
501	24.2	15.6	56.0	2.0	2.0
202	24.7	16.7	55.0	-	-
68	24.2	15.3	55.5	2.6	2.5
66	25.0	16.3	54.5	2.0	2.2
34	24.3	16.5	55.0	2.1	2.1
30	24.4	15.0	55.5	2.2	2.9
12.8	22.6	15.8	57	2.8	1.8
7.4	22	14.0	57	3.5	3.5
5.4	20	14.0	56	-	-
Keten-quartz R.V.					
56.	23.	16.0	56.0	2.8	2.2
94	2.25	16.0	56.5	3.0	2.0
Diazomethane-Pyrex R.V.					
	25.0	25.0	45.0	4.0	2
Mean of the first series:					
	23.6	15.4	56.0	2.4	2.4

CHAPTER VI

REACTION OF METHYLENE WITH TETRAFLUOROETHYLENE

Summary. The reaction of methylene generated from keten with tetrafluoroethylene has been studied. Two products found have been ascribed to 1,1,2,2 tetrafluorocyclopropane - $CF_2\overset{CH_2}{<}CF_2$ and 1,1,3,3 tetrafluoropropylene $CF_2 = CH-CF_2H$. The reaction scheme has been postulated in accordance with the experimental results. It suggests that no insertion into the C-F bond occurs. Methylene reacts only with the double bond to form tetrafluorocyclopropane, which isomerises by the nepture of the CF_2-CF_2 bond and a hydrogen shift. No fluorine migration takes place.

Experimental. The kinetic apparatus was identical to that described in Chapter 2.2. The high pressure experiments were carried out in sealed Pyrex ampoules of ~3cc. volume. The volume of each ampoule was determined by weighing it with water. Only two products were found using two columns: a column packed with 5% squalane (No. 1 in table 2.3) and a second one filled with alumina poisoned with 1% of dinonylphthalate. The latter column was used for quantitative analysis.

As none of the expected products had been described in the literature, the only way of identifying them was i.r. analysis. The i.r. spectra of both products found are included in Figs. 12 and 13.

Results. A reaction scheme that accounts for the occurrence of the products found and their distribution at different pressures may be represented as follows:

$$CH_2CO + h\nu \longrightarrow CH_2 + CO \qquad (a)$$

$$CH_2 + CF_2 = CF_2 \xrightarrow{k_1} CF_2(CH_2)CF_2^{*} \qquad (1)$$

$$CF_2(CH_2)CF_2^{*} + M \xrightarrow{k_{deact.}} CF_2(CH_2)CF_2 + M \qquad (2)$$

$$CF_2(CH_2)CF_2^{*} \xrightarrow{k_{isom.}} CF_2 = CH\text{-}CF_2H \qquad (3)$$

Table 6.1 gives the data on the change of the % yield of the cyclic product in the pressure range 90-4700mm.Hg. The increase in this value with the increase of pressure suggests that process (2) competes with reaction (3). The steady state equation applied to the reaction scheme yields:

$$\frac{[CF_2 = CH\text{-}CF_2H]}{[CF_2(CH_2)CF_2]} = \frac{k_{isom.}}{k_{deact.}M}$$

The plot of the ratio of yields of products against the reciprocal of pressure should, according to the above scheme, be a straight line. The plot obtained from the experimental data is linear, except at low pressures where a slight curvature occurs, (Fig. 11.) As only two points deviate from the straight line it is difficult to decide whether the energy spread effect is responsible for this.

The gradient of the line equal to $\frac{k_{isom.}}{k_{deact.}}$ was estimated as 275cm. The fact that the intercept of this line is equal to zero, which corresponds to a value of 100% of the cyclic compound yield, suggests that only addition to the double bond occurs at infinite pressure.

The expression for the yield of the cyclic product at pressure M assuming the above values for $\frac{k_{isom.}}{k_{deact.}}$ and $f\ \begin{matrix} CH_2 \\ / \quad \backslash \\ CF_2 - CF_2 \end{matrix}$ is:

$$\begin{matrix} CH_2 \\ / \quad \backslash \\ CF_2 - CF_2 \end{matrix} = f\ \begin{matrix} CH_2 \\ / \quad \backslash \\ CF_2 - CF_2 \end{matrix} = \frac{100}{1 + \frac{k_{isom.}}{k_{deact.}M}} = \frac{100}{1 + \frac{275}{M}}$$

The values of $R\ \begin{matrix} CH_2 \\ / \quad \backslash \\ CF_2 - CF_2 \end{matrix}$ calculated from the above expression are incorporated in table 6.1. Fig. 10 represents the data from this table: the line is drawn from the calculated data, the points are the actual experimental values. The agreement between the two sets of values is good. The fact that only one product of isomerization was found and its structure is more likely to be $CF_2 = CH\text{-}CF_2H$ than $CF_2 = CF\text{-}CH_2F$ implies that the isomerization of tetrafluorocyclopropane involves rupture of the $CF_2\text{-}CF_2$ bond and migration of the hydrogen atom bound originally to the adjacent carbon. This is conceivable, as the $CF_2\text{-}CF_2$ bond is probably weaker than the $CF_2\text{-}CH_2$ bond (the $CF_2\text{-}CF_2$ bond is weaker than the $CH_2\text{-}CH_2$ bond) and also the movement of hydrogen atom is intuitively more feasible than that of the heavier fluorine.

Effect of the reactants ratio on the distribution of products. In order to find whether the composition of the reaction mixture affects the distribution of products a few experiments were carried out using different ratios of reactants, the total pressure and the time of irradiation being the same. Table 6.2 gives the results obtained.

Table 6.2 *

[Ketene] / [C_2F_4]	% Yield of CH_2 / CF_2 — CF_2
1 : 1	4.9
1 : 1	5.4
1 : 2	7.0
1 : 3	9.1
1 : 5	10.0
1 : 9	11.2
1 : 10	11.4

*All experiments were carried out at 29.4cm.Hg.
Time of irradiation - 30 mins.

The results show a marked increase in the CH_2 / CF_2 — CF_2 yield with the increase of the C_2F_4 fraction in the reaction mixture, the yield reacting a constant value at ~8 fold excess of C_2F_4. The above finding can be ascribed to a different efficiency in deactivating the excited tetrafluorocyclopropane of the two components of the mixture, C_2F_4 being more efficient than keten.

Effect of the time of irradiation on the distribution of products.

The results of a few experiments carried out with different times of irradiation, maintaining the same total pressure and the same reactant ratio are shown in the table below;

Table 6.3 *

Time of irr. (min.)	% yield of $CF_2 = CH-CF_2H$
20	84.6
46	84.4
75	84.3
92	79.1
120	80.0
120	80.5

*Total pressure in all experiments 51.1mm. ± 1mm.

$$\frac{[\text{Keten}]}{[C_2F_4]} = 1 : 9$$

The small decrease in the yield of tetrafluoropropylene when the time of photolysis exceeds 75 min. can be explained by the occurrence of the secondary reactions of methylene with the products, which would be faster for the unsaturated tetrafluoropropylene, depleting this compound to a larger extent than the saturated tetrafluorocyclopropane.

Table 6.1 Reactions of tetrafluoroethylene (Keten as the methylene source)

$$\frac{k_{isom.}}{k_{deact.}} = 275\text{cm.} \qquad R_{calc.} = \frac{100}{1 + \frac{275}{M}}$$

Pressure (cm.Hg.)	$\frac{1}{\text{Pressure}}$ (cm^{-1})	Time of photolysis (min.)	% yield of $CH_2 / \backslash 2$ $CF_2 - CF_2$ Exp.	% yield of $CH_2 / \backslash 2$ $CF_2 - CF_2$ calc.	$\frac{[CF_2 = CH\text{-}CHF_2]}{CH_2 / \backslash 2 \; CF_2 - CF_2}$
470	0.0021	30	59.6	63	0.68
415	0.0024	30	59.6	60	0.68
350	0.0028	30	55	56	0.82
334	0.0030	33	60	55	0.66
267	0.0037	30	47.5	49.4	1.1
254	0.0039	40	49.2	49	1.06
205	0.0049	31	44.0	43	1.3
185	0.0054	36	44.8	40.5	1.23
166	0.0060	30	40.0	37.8	1.5
148	0.0067	30	39.8	35	1.5
125	0.0080	30	33.68	31.2	2.0
84	0.0120	37	24.0	23.4	3.2
76.7	0.0130	30	21.0	21.8	3.8
73.4	0.0136	30	20.0	21.5	4.0
63.6	0.0158	30	19.0	18.7	4.3
60.0	0.0167	64	180	17.9	4.6
51.0	0.0196	46,75,20	15.6	15.6	5.4
44.6	0.0224	34	12.8	13.5	6.8
40.9	0.0244	30	13.0	13.0	6.7
34.9	0.0287	30	12.5	11.2	7.0
30.0	0.0333	30	11.2	9.8	7.9
25.5	0.0393	30	9.8	8.5	9.7
9.1	0.110	30	3.0	2.4	32.4

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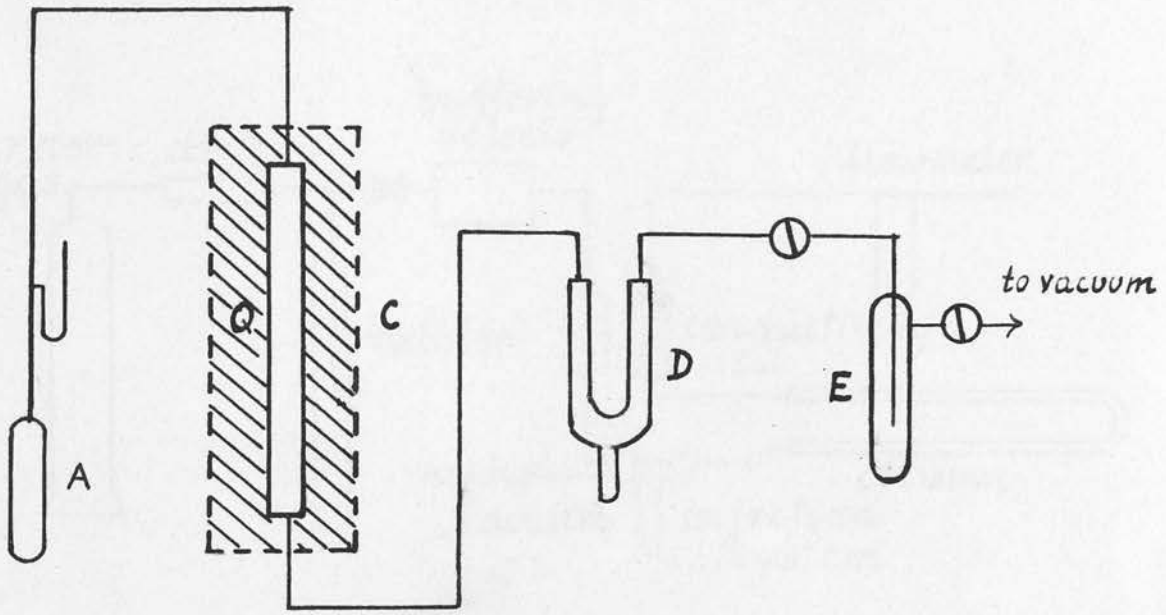

FIG.1. KETEN APPARATUS

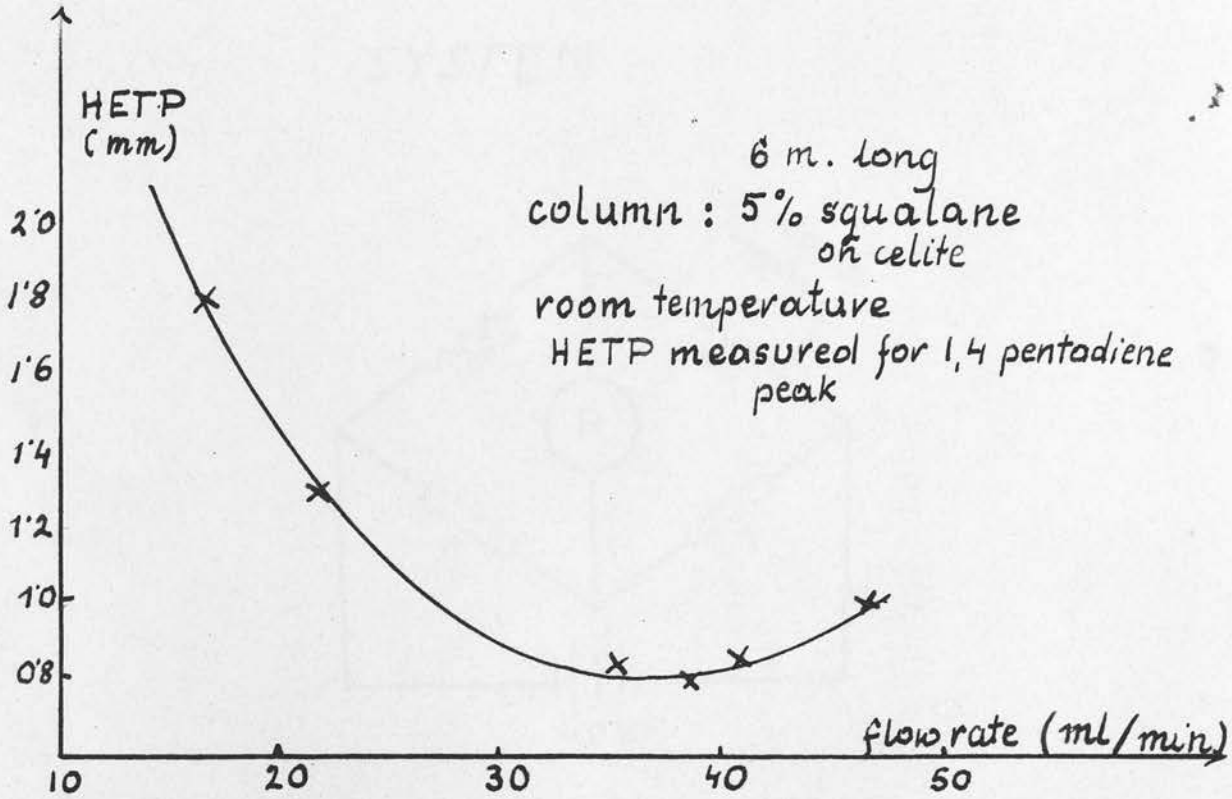

FIG. 2. CHANGE OF HETP WITH F.R.
FOR COLUMN 1.

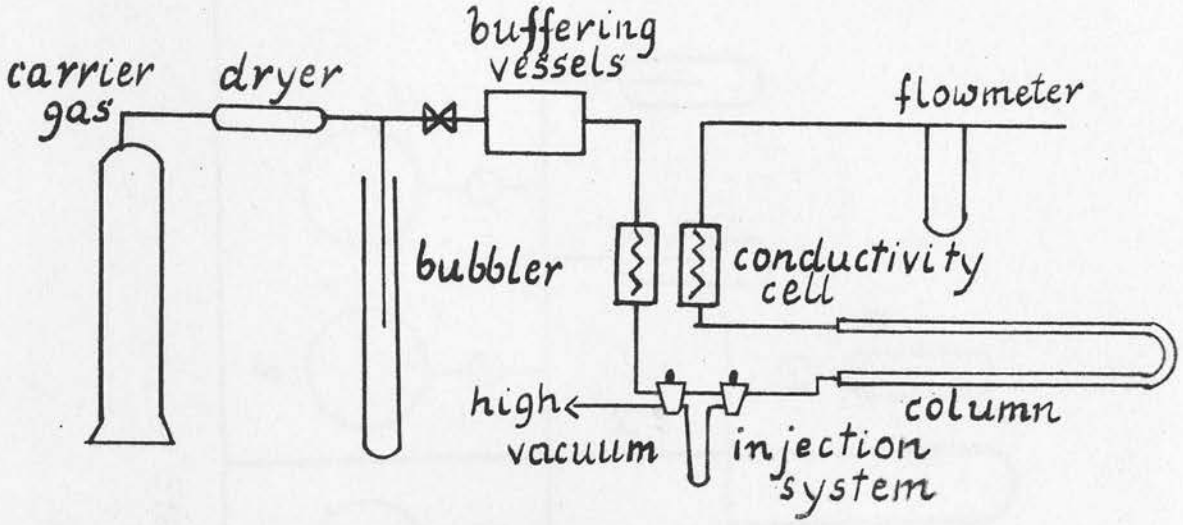

FIG.3. SCHEMATIC DIAGRAM OF CHROMATOGRAPHY SYSTEM

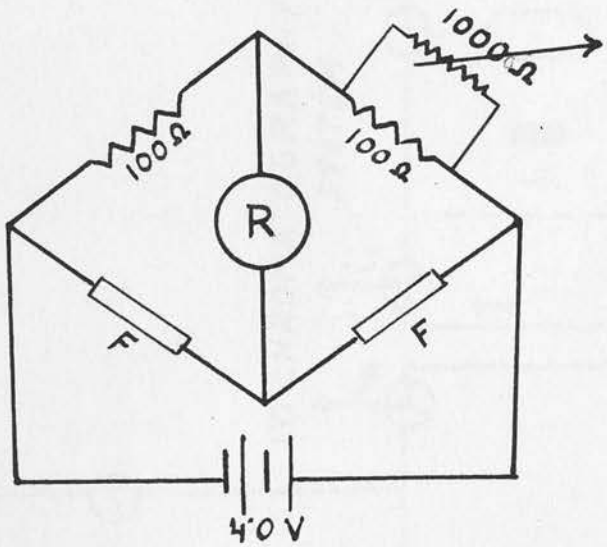

FIG. 4. CIRCUIT FOR KATHAROMETER

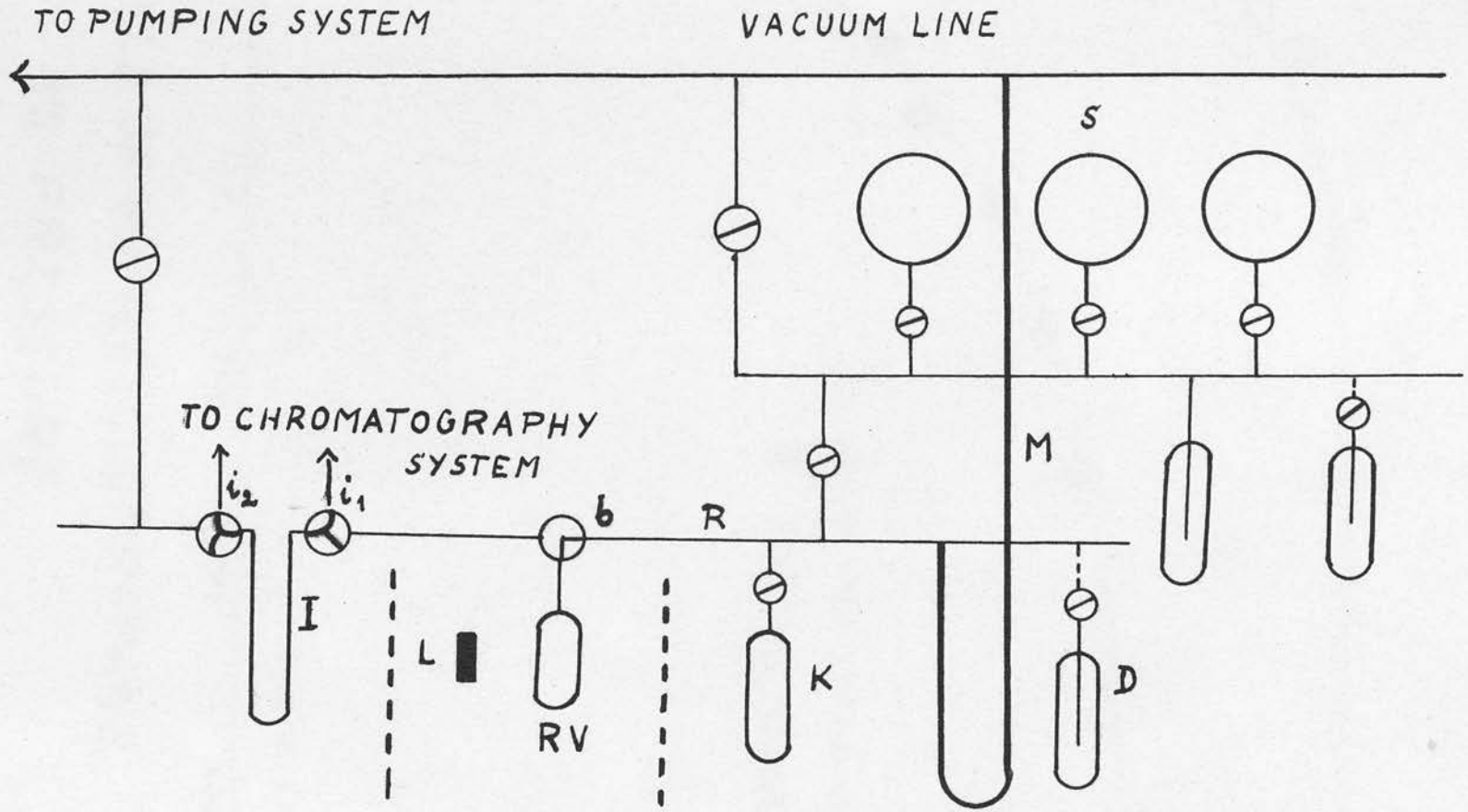

FIG.5 APPARATUS

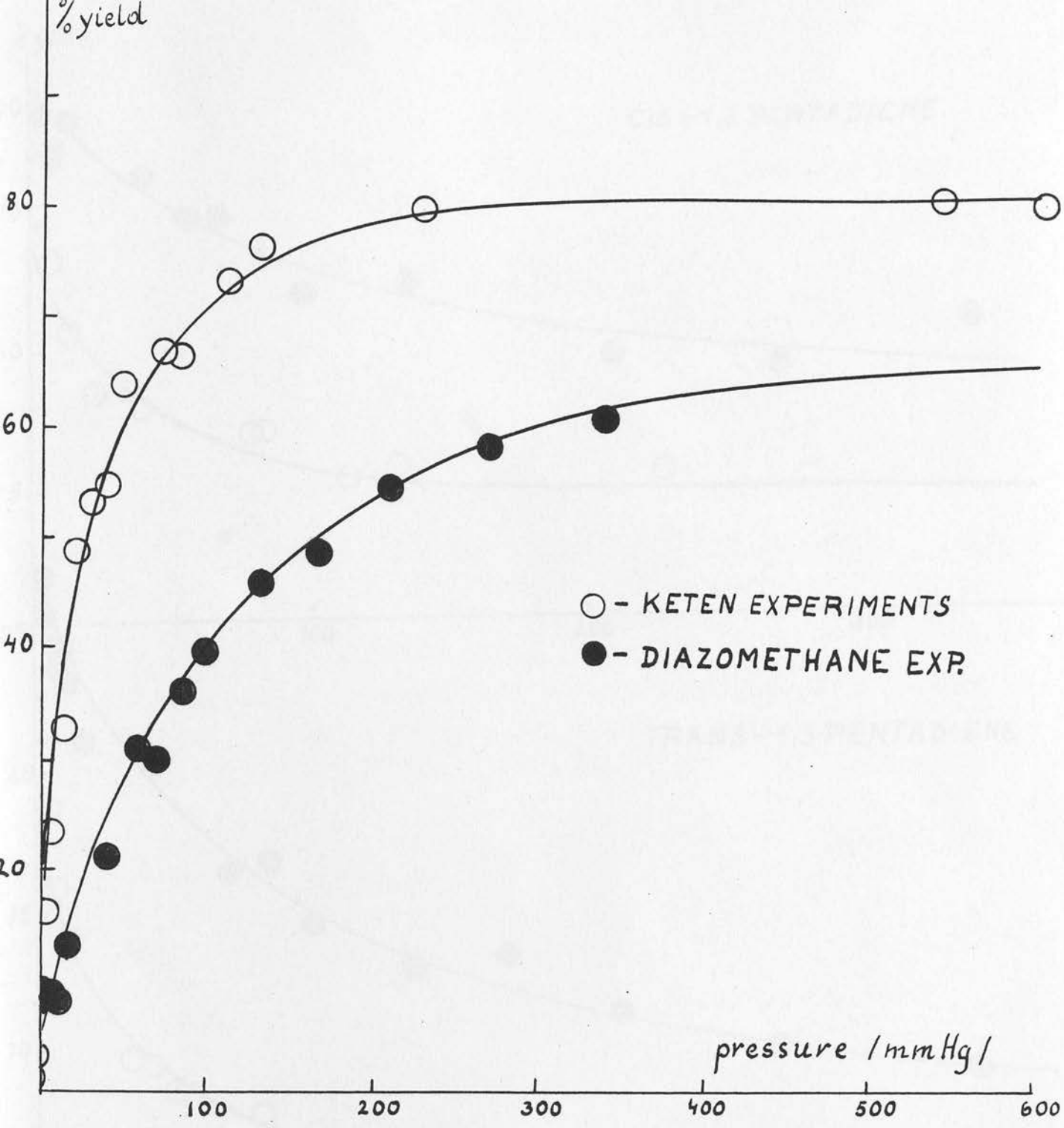

FIG.6. YIELD OF VINYLCYCLOPROPANE VS PRESSURE

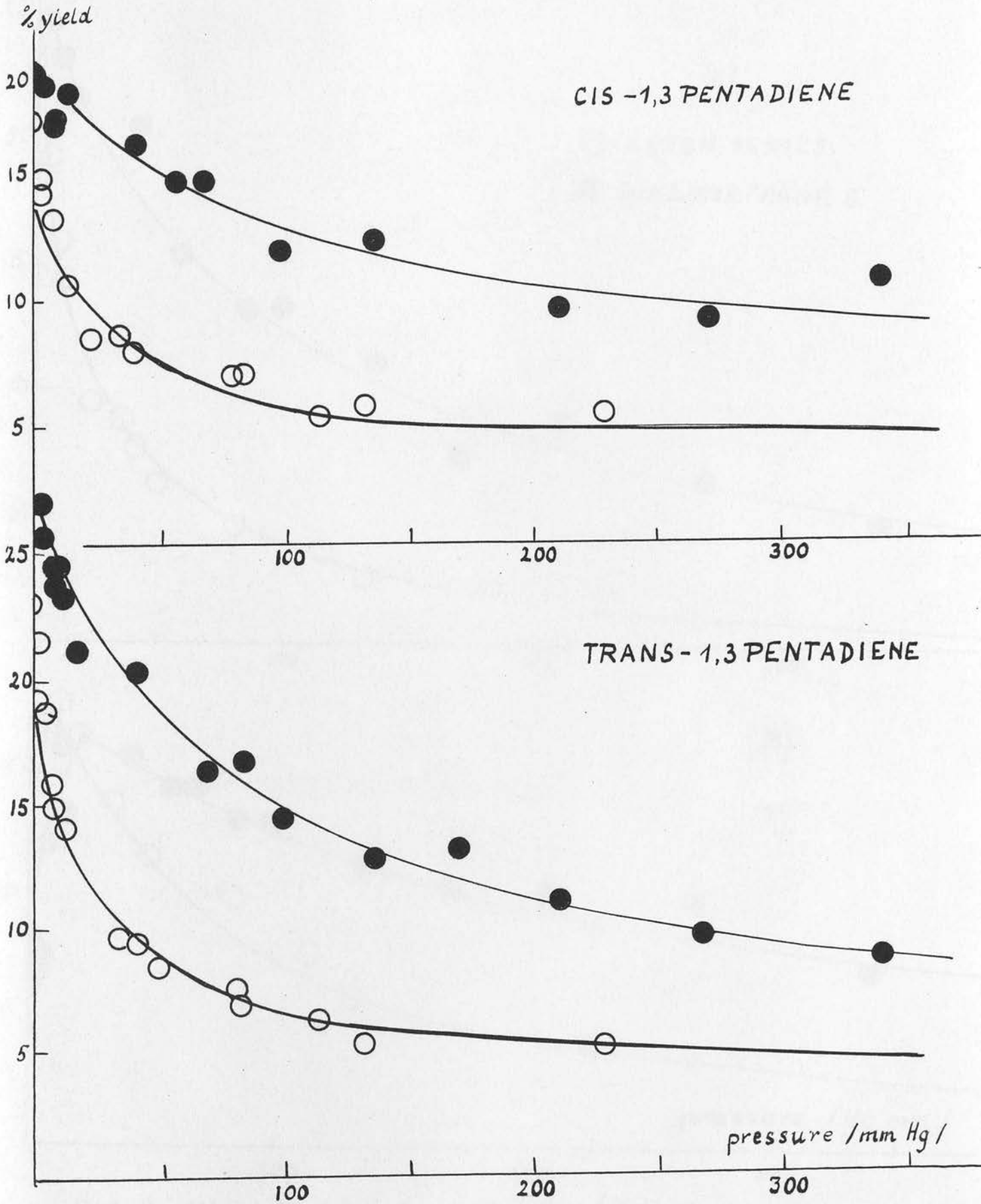

FIG.7. YIELD OF 1,3 PENTADIENES VS. PRESSURE

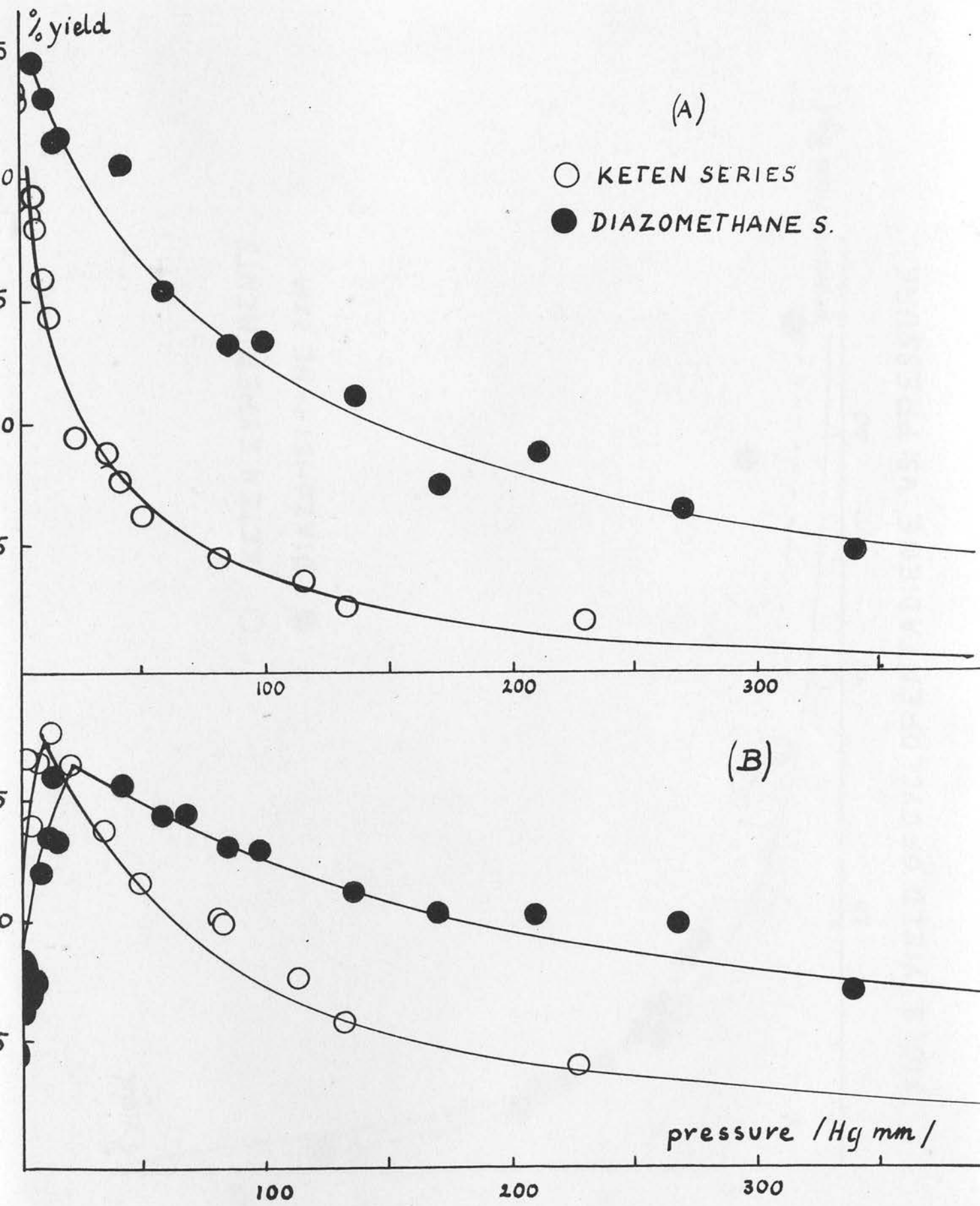

FIG. 8. YIELD OF (A) 1,4 PENTADIENE (B) CYCLOPENTENE VS. PRESSURE

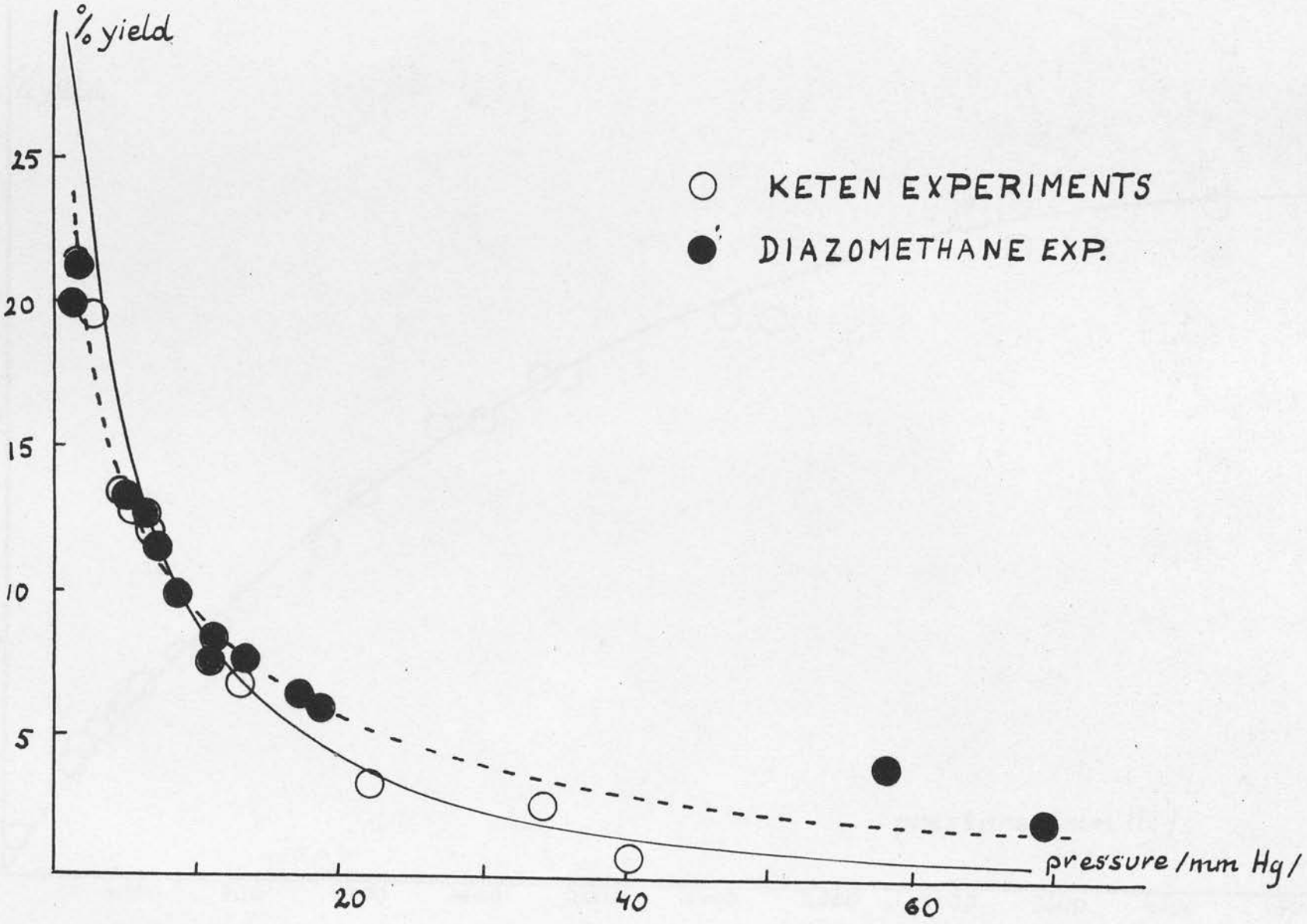

FIG. 9. YIELD OF CYCLOPENTADIENE VS. PRESSURE

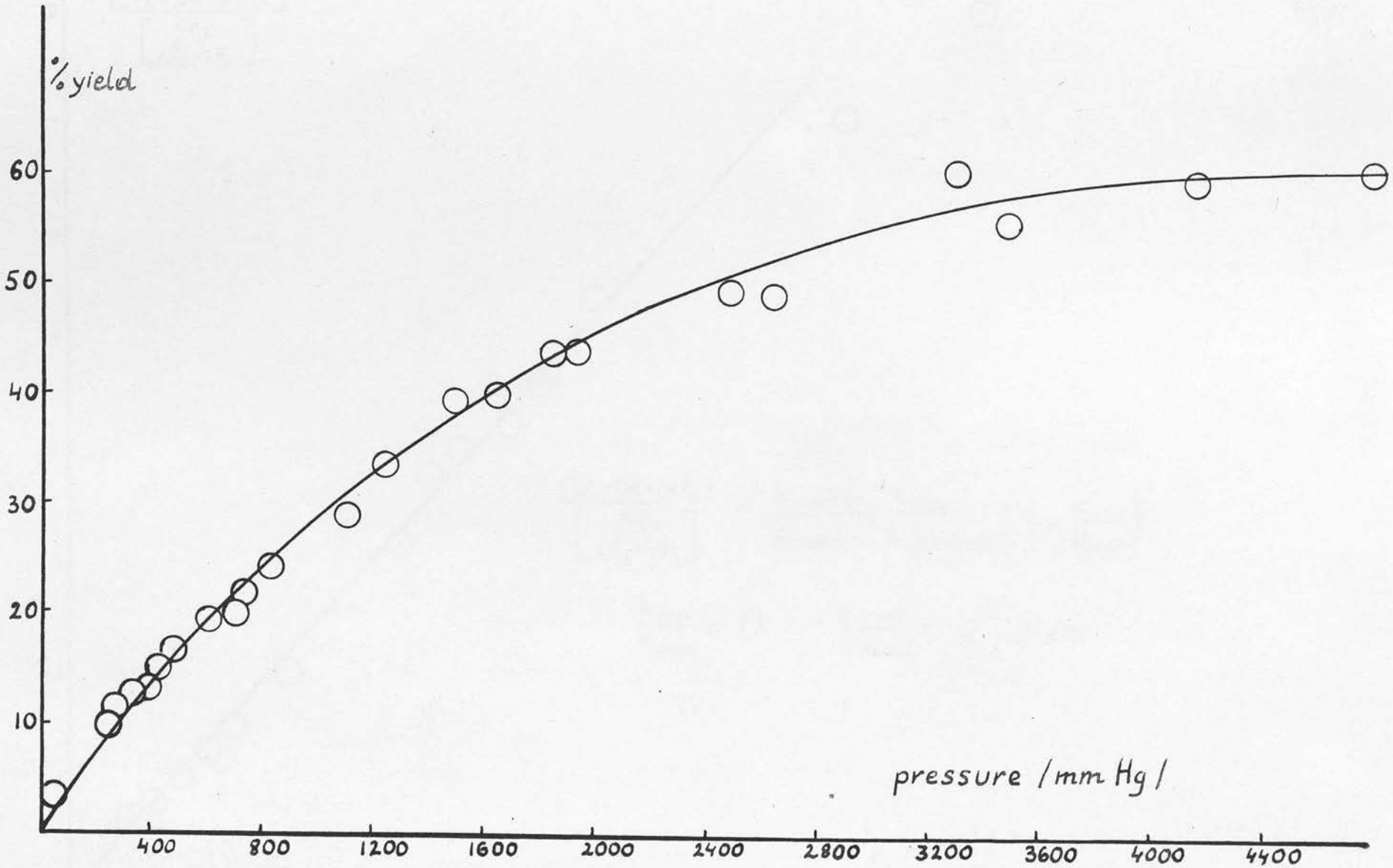

FIG. 10. YIELD OF TETRAFLUOROCYCLOPROPANE VS PRESSURE

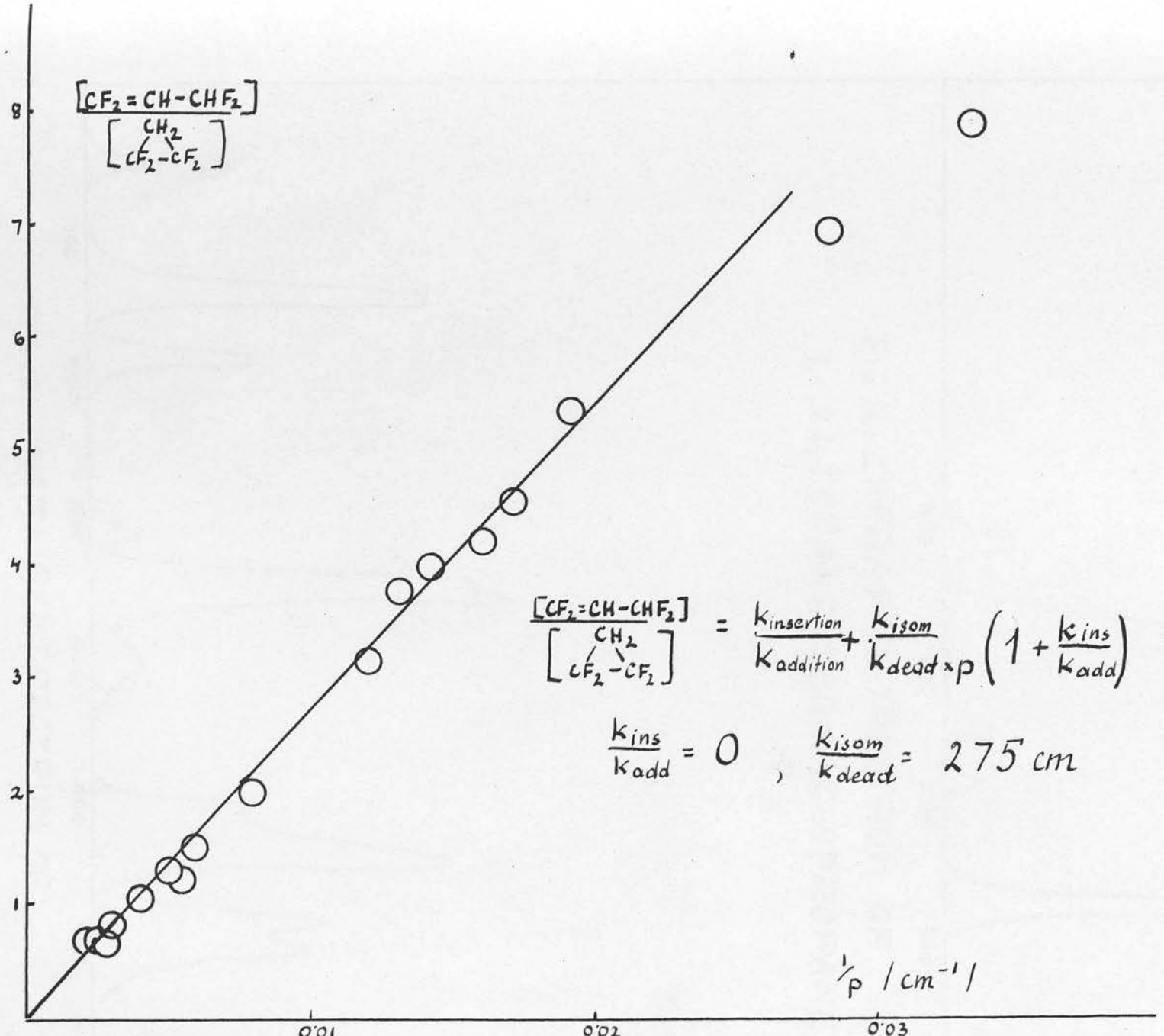

FIG.11. RATIO OF YIELDS OF PRODUCTS VS RECIPROCAL OF PRESSURE

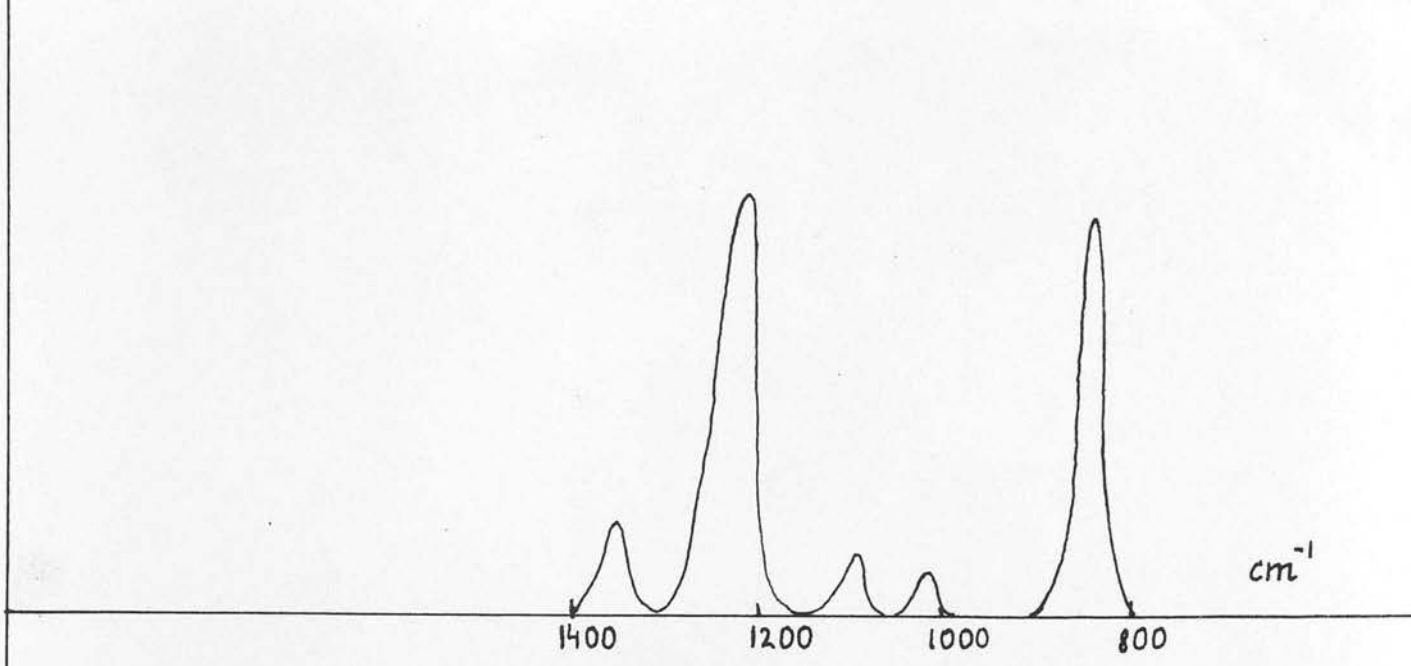

FIG 12. INFRA-RED SPECTRUM OF
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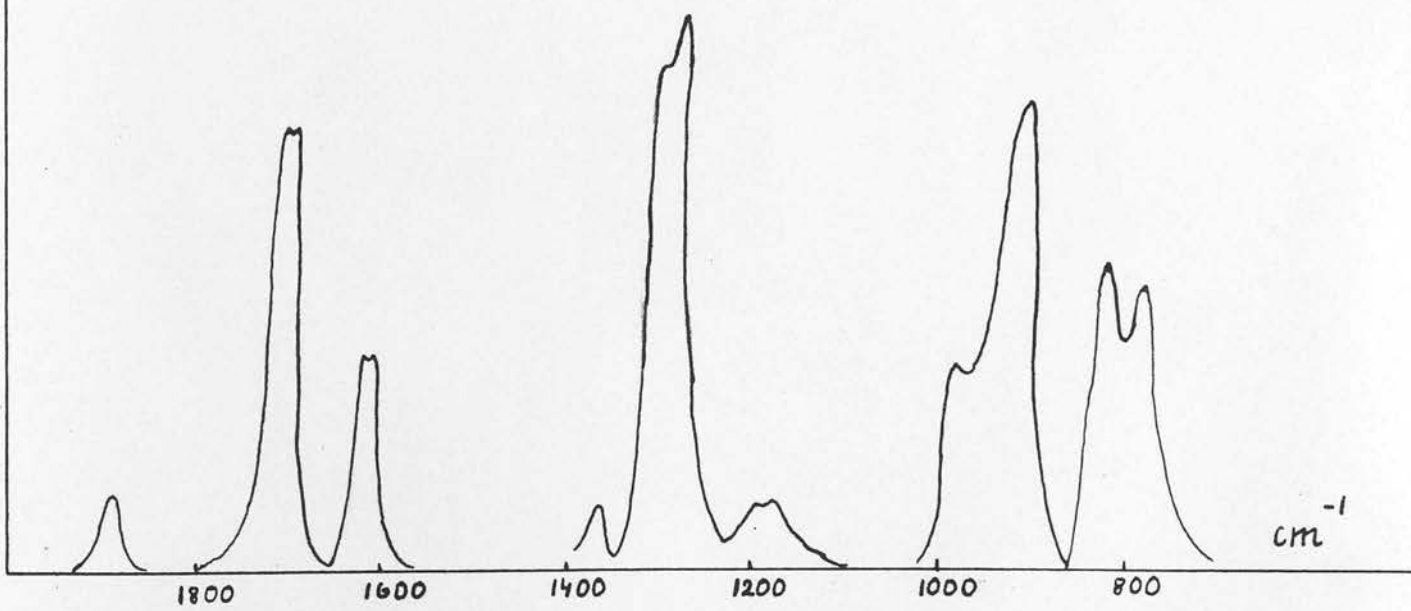

FIG 13. INFRA-RED SPECTRUM OF
1,1,3,3, TETRAFLUOROPROPYLENE